PB-233 641

AN ION-EXCHANGE PROCESS FOR RECOVERY OF CHROMATE FROM PIGMENT MANUFACTURING

MINERAL PIGMENTS CORPORATION

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JUNE 1974

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EPA-670/2-74-044
June 1974

AN ION-EXCHANGE PROCESS FOR RECOVERY OF CHROMATE FROM PIGMENT MANUFACTURING

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Project 12020 ERM
Program Element 1BB036

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OFFICE OF RESEARCH AND DEVELOPMENT
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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before comple

1. REPORT NO.
EPA-670/2-74-044

2.

3. PB 233 641

4. TITLE AND SUBTITLE
AN ION-EXCHANGE PROCESS FOR RECOVERY OF CHROMATE FROM PIGMENT MANUFACTURING

5. REPORT DATE
June 1974; Issuing Date

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
Donald J. Robinson, Harold E. Weisberg, Glenn I. Chase, Kenneth R. Libby, Jr., and James L. Capper

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Mineral Pigments Corporation
7011 Muirkirk Road
Beltsville, Maryland 20705

10. PROGRAM ELEMENT NO.
1BB036:ROAP 21 AZQ:Task 03

11. CONTRACT/GRANT NO.
12020 ERM

12. SPONSORING AGENCY NAME AND ADDRESS
National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final Report

14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT
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From these laboratory studies, a full-scale ion-exchange treatment plant was designed, constructed, and demonstrated. The chromate composition of the plant effluent is being reduced from 2700 ppm to one to two ppm.

The treatment system was designed to treat 60 gallons per minute of influent and to discharge an effluent which is within statutory limits for pH and for heavy metal content. The plant was designed to require minimal manual supervision. The steps in treatment and in resin regeneration are performed automatically and the control system is interlocked to make it fail safe. Operators are required only to make up regeneration solutions, to clean pump strainers and filters, to answer to alarms and occasionally to differentiate between turbidity and color as seen by by colorimeter.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Industrial waste treatment *Ion exchangers *Pigments *Materials recovery Waste treatment Adsorption Chromium	*Wastewater treatment Zinc *Chemical manufacturing wastes	13B

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INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

18. DISTRIBUTION STATEMENT
Release to public

19. SECURITY CLASS *(This Report)*
Unclassified

20. SECURITY CLASS *(This page)*
Unclassified

21. NO. OF PAGES
102

22. PRICE
$4.50

☆ U. S. GOVERNMENT PRINTING OFFICE: 1974-757-584/5325 Region No. 5-11

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment -- air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

The studies for this report were undertaken to demonstrate the suitability of an ion-exchange system for the treatment of concentrated chromium containing rinse waters from the manufacture of zinc-yellow pigment. The system removes over 99% of chromium thereby preventing contamination of the receiving waters while at the same time permitting recycling of the chromium, a valuable resource, to the succeeding batch of pigment. The system also permits recovery of the zinc contained in the rinse water in the form of a saleable by-product, zinc carbonate. This new technology could have a major effect on the industry's efforts to protect our Nation's water resources.

A. W. Breidenbach, Ph.D.
Director
National Environmental
Research Center, Cincinnati

ABSTRACT

Strongly basic ion-exchange resins have been shown to exhibit a preference for dichromate over many other anions in water solution. Laboratory studies were conducted to show that this ion preference could be used to remove chromate from waste waters which were discharged from a zinc yellow pigment manufacturing plant. It was also shown that the recovered chromate solution could be recycled into product manufacture without sacrificing product quality.

From these laboratory studies, a full-scale ion-exchange treatment plant was designed, constructed, and demonstrated. The chromate composition of the plant effluent is being reduced from 2700 ppm to one to two ppm.

The treatment system was designed to treat 60 gallons per minute of influent and to discharge an effluent which is within statutory limits for pH and for heavy metal content. The plant was designed to require minimal manual supervision. The steps in treatment and in resin regeneration are performed automatically and the control system is interlocked to make it fail safe. Operators are required only to make up regeneration solutions, to clean pump strainers and filters, to answer to alarms and occasionally to differentiate between turbidity and color as seen by the colorimeter.

This report was submitted in fulfillment of Project Number 12020 ERM, by Mineral Pigments Corporation under the (partial) sponsorship of the Environmental Protection Agency.

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ACKNOWLEDGMENTS

We would like to acknowledge the kind assistance of Mr. Sam Griggs, formerly of the Charlottesville, Va. Office of E.P.A., our first project officer; Mr. John Ciancia, Mr. Bernard Hornstein and Mr. Richard Tabakin, all of the Edison Water Quality Research Laboratory, Edison, N. J. who have worked closely with us in bringing the project to a successful completion. We would like to thank Mr. Rodney L. Gast, Dr. Jesse Williams, Mr. Charles Hodge and Mr. David L. Seal for their careful laboratory work, Mr. Donald W. Agee and Mr. John D. Meininger for their assistance in wiring and instrument installation, and Mr. John Phillips for his assistance in preparing many of the drawings.

We acknowledge the help of Mr. Charles T. Dickert and Mr. Robert Kunin of Rohm and Haas Co. and Mr. James C. Hessler, Mr. Tony Diblik and Mr. William Ward of Nalco Chemical Co. all of whom made many helpful suggestions while the plant was in its design stages. Also Mr. Robert Gerster of Jacoby-Tarbox who helped in the selection of an appropriate filter to detect the sodium dichromate color and for his determination of the path length required in the colorimetry to give the required 1 ppm sensitivity.

Our pleasure in all of this is diminished by the fact that Dr. Harold E. Weisberg and Mr. James L. Capper both of whom died before the project's completion cannot share in this satisfaction.

CONCLUSIONS

1. Either of two strongly basic ion-exchange resins can be used successfully to reduce the chromate content of pigment plant effluent from 2700 ppm to less than one ppm of total chromium expressed as Cr.

2. The ion-exchange resins can be regenerated with an alkaline salt solution. In this plant, the salt used, potassium chloride, is a raw material in manufacture of zinc yellow pigment. It is "borrowed" long enough to accomplish the regeneration; then it is returned to the manufacturing unit, along with the recovered dichromate, for re-use.

3. The recovered chromate solution can be used in the manufacture of some chromate pigments without degradation of the product quality. This, of course, is the key to the complete success of the plant operation.

4. This plant has been designed so that steps in the treatment and in the resin regeneration cycles follow automatically. These steps are quite dependably controlled by color, tank level, time, and pH.

5. Operators are required only to make up solutions, clean filters, answer alarms, and occasionally differentiate between color and turbidity as seen by the colorimeter.

RECOMMENDATIONS

This plant has been limited to treatment of waste waters recovered from the manufacture of zinc potassium chromate. The waste water contains zinc and chromate ions and high concentrations of sodium chloride. The ion exchange resin, in the chloride form, is successful in removing chromate in exchange for chloride. Other chromate pigment wastes might contain sodium sulfate, sodium nitrate, or sodium acetate. Additional laboratory work would be necessary to demonstrate whether the resin will adsorb chromate preferentially in competition with high concentrations of these ions and whether an appropriate use could be found for the recovered chromate solution.

Were we to start anew, we would consider having the bottom diffuser openings through the tank bottom with the support screens external and with each opening individually valved. This would enable one to make screen repairs without removing the resin from the ion-exchange column and would make a uniform up-flow during backwash more easily attainable. It does present the possibility of an inactive area on the tank floor which would collect exhausted resin. Some further study of the design would be helpful.

More work with level sensing devices will be required. We have evaluated the applicability of a number of conductance and capacitance level probes and for some uses we have not overcome their limitations. A study of sonic probes is in process.

The polyester screens used in the diffuser openings are quite succesful in retaining the resin beads while permitting uniform flow. Their most serious limitation is that they fatigue with continued flexing and they eventually rupture. Monel cloth is currently being evaluated. This system does require periodic maintenance and merits further study.

INTRODUCTION

Chromate, a deep yellow-colored, ion, in dilute water solution, is a necessary by-product of chromate pigment manufacturing. The commercial manufacture of chromium containing pigments can be represented by chemical reactions such as equations (1) and (2). Equation (1)

$$Na_2Cr_2O_7 + S \rightarrow Cr_2O_3 + Na_2SO_4 \qquad (1)$$

$$Na_2Cr_2O_7 + 2MO + 2HY \rightarrow 2MCrO_4 + 2NaY + H_2O \qquad (2)$$

represents an over-simplified version of the reduction of sodium dichromate by sulfur (carbon could also be used) to form the green pigment chromium oxide and a water soluble salt, which in this case is sodium sulfate. Equation (2) represents the preparation of the yellow chromate pigments. M is a heavy metal such as lead, zinc, barium, strontium, or calcium. Y is an anion such as chloride, nitrate, or acetate. Lead and barium chromates are only very slightly water soluble, but strontium, calcium, and zinc chromates exhibit an appreciable solubility in water. Because of this solubility, or because the reactions as depicted by equations (1) and (2) above may not proceed quantitatively to the right, the filtrates and wash liquors from the precipitation and recovery of these pigments contain chromate ions together with the salts sodium chloride, sodium sulfate, sodium nitrate, or sodium acetate.

Waste waters containing chromium in excess of 0.5 ppm may not be discharged into surface streams. The current practice is to collect these filtrates and wash liquors and either dispose of them in deep wells[1] or to acidify and reduce the resulting dichromate solution with sulfur dioxide or sodium sulfite. The chromium is then precipitated as a hydrous oxide and is discarded in a land-fill area. The overall reaction of this latter method may be represented by equation (3). This practice

$$Na_2Cr_2O_7 + 3Na_2SO_3 + H_2SO_4 + (2+x)H_2O \rightarrow 2Cr(OH)_3.xH_2O + 4Na_2SO_4 \quad (3)$$

is unsatisfactory, first because it is wasteful, secondly because the hydrous chromium oxide is a light bulky precipitate which does not settle readily. The resulting supernatant solution is often turbid. A third problem is that, in the presence of acetate or chloride ions, coordination compounds are frequently formed which do not precipitate to yield a water-white effluent. Under these conditions the pigment plant effluent is frequently green or pale blue-green and contains color and chromium in excess of statutory limits.

We have proposed and will describe here a water treatment plant which will remove chromate from plant effluent liquors. This plant utilizes ion-exchange resins which exhibit a preference for dichromate over the other anions present in the waste water. The dichromate is adsorbed on the ion-exchange resin and may be recovered from the resin and re-used in the pigment manufacturing process.

The chromate ion exists as a monochromate. On acidification it is converted to chromic acid (monochromic acid.) Two moles of chromic acid can then lose a mole of water and become a dimer or dichromic acid.

$$2H_2CrO_4 - H_2O \rightarrow H_2Cr_2O_7 \qquad (4)$$

This process can continue, forming trichromic acid, tetrachromic acid, etc.[2] We will confine our discussion to chromate ions, existing in neutral or alkaline solutions, and to dichromate ions, existing in acidic solutions. We will report all chromium analyses as sodium dichromate, dihydrate ($Na_2Cr_2O_7.2H_2O$), for ease of intercomparison, even though no dichromate ion may be present in, for instance, an alkaline regenerant solution or a neutral filtrate from the zinc yellow pigment manufacturing operation.

The adsorption of dichromate on the resin is favored by low pH conditions and is represented in equation (5). The recovery of the chromate is accomplished at a high pH and may be represented as in equation (6).

$$Cr_2O_7^{=} + 2ResinCl \rightarrow (Resin)_2Cr_2O_7 + 2Cl^- \qquad (5)$$

$$(Resin)_2Cr_2O_7 + 2OH^- + 2Cl^- \rightarrow 2Resin\ Cl + 2CrO_4^{=} + H_2O \qquad (6)$$

The original work on this process as reported by Hesler[3] and by Hesler and Oberhofer[4,5] was generally limited to chromate concentrations of 30 to 100 ppm such as result from the discharge from cooling towers or from boiler blow-down. Our initial interest was to determine whether this ion-exchange resin would withstand dichromate concentrations up to 2700 ppm and to determine whether the adsorption would be specific for dichromate in the presence of much higher concentrations of other alkali metal salts.

Other questions were immediately apparent. At what concentration can the recycled chromate be recovered? Does the recovered solution, which is of necessity high in chloride ion concentration, affect the color or chemical properties of the pigment into which it is recycled? Can the ion-exchange resin be repeatedly regenerated in such a manner as to always yield a water-white effluent, or will some further treatment procedure, e.g., reduction-precipitation, be required?

When we discuss the chromium content of treated waste water we will express the concentration as ppm of chromium (Cr) and will understand that this is total chromium in all oxidation states, and in water soluble as well as insoluble forms.

At the time of our grant application the effluent specifications were as listed in Table 1. Since that time there has been considerable discussion that the total chromium content of industrial effluents should be under 0.5 ppm total chromium and perhaps as low as 0.05 ppm of hexavalent chromium.[6]

Table 1. 1969 EFFLUENT SPECIFICATIONS

Suspended solids	400 ppm max
Turbidity	300 ppm max
Color	400 ppm max
B.O.D.	100 ppm max
pH	5.5 to 8.5
Oil	30 ppm max
Cr	1 ppm max

While the process to be described here has been shown to be satisfactory to attain the 1.0 ppm chromium specification, some post treatment would be required to attain the 0.05 ppm level. An effluent of 0.05 ppm would require an extremely complete regeneration of the ion-exchange resin. Also, our control step to signal the need for secondary treatment (a second column in series) is predicated upon the appearance of color in the effluent. The appearance of color is equivalent to a concentration far in excess of 0.05 ppm of hexavalent chromium.

In this report we will describe the laboratory studies which were undertaken to answer the above questions regarding the resin performance and regarding the properties of the recovered chromate solution. We will describe the process of scale-up from the bench unit to our final plant design. We will describe the design of the water treatment plant and the details of pH, color, flow and level control. We will describe our experience in the first twelve months of plant operation and give indications of the equipment costs and the prospects for amortizing this expense.

LABORATORY EVALUATION

HIGH DICHROMATE CONCENTRATIONS

The original work on dichromate removal by ion-exchange was generally limited to chromate concentrations of 30 to 100 ppm. Our first interest was to discover whether this ion-exchange resin would withstand concentrations up to 2700 ppm, and to discover whether the adsorbtion would be specific for dichromate in the presence of much higher concentrations of other alkali metal salts.

We obtained a sample of Dowex "SBR" resin from Nalco Chemical Company[7] and tested it on filtrates from our zinc yellow and our chromium oxide processes. The influent to the resin contained 2.7 grams of $Na_2Cr_2O_7.2H_2O$/ liter. The effluent from the resin was water-white or pale yellow, depending on the rate at which the filtrate was allowed to flow through the resin column. In these preliminary or survey tests we showed that chromate concentrations as high as 2700 ppm could be adsorbed by the resin nearly quantitatively, as determined visually.

In the laboratory work which followed we at one time exposed the resin to 11,000 ppm dichromate and later in plant operation the resin was accidentally exposed for a brief period to 15,000 ppm dichromate with no apparent damage.

RESIN SPECIFICITY

The initial survey was extended to include filtrates which contained calcium and strontium as well as zinc as heavy metals, and nitrate and acetate in addition to chloride and sulfate anions. As long as the pH was maintained in the 3 to 4 region, the heavy metals presented no problem and the resin showed an apparent specificity for dichromate over all of the other anions tested. The balance of this report will, however, be limited to a discussion of our experience with zinc as the heavy metal cation and chloride as the competing anion.

RESIN REGENERABILITY

We next attempted to study the regeneration process. An exhausted column was flushed with water, then covered with the recommended[8] regenerant solution. Small portions of the regenerant were removed every fifteen minutes. The pH of each sample was recorded and an aliquot portion was analyzed for its chromate content iodometrically. The analytical procedure for the chromium analysis and the details of this study are reported in Appendices A and B respectively. The maximum concentration of chromate in the recovered solution was not obtained until the pH of the regenerant solution exceeded 8.5 after it was passed through the dichromate-containing resin. The pH of the recovered solution then rose sharply from that pH, indicating that the dichromate on the column had apparently been neutralized, or converted to chromate, and the concentration of chromate in the recovered solution then reached its maximum value and dropped quite sharply.

Starting with freshly prepared regenerant solution and causing the regenerant to flow through the column in a single pass one will obtain a concentration relationship of the general shape illustrated in Figure 1. If, however, one recirculates the alkaline regenerant through the resin until the acidity of the dichromate ion which has been adsorbed on the resin has been neutralized one can displace the curve toward the left axis as illustrated in Figure 2.

Further, now, if one re-uses volumes III and IV from one regeneration as volumes I and II, respectively, of the next succeeding regeneration one can obtain a relationship as shown in Figure 3. In this manner we succeeded in maximizing the concentration of the recovered chromate solution for re-use and yet held the total regenerant volume and the time required for satisfactory regeneration to a minimum.

By placing a second resin column in series with the first to collect the dichromate which bleeds from the first column it is possible to load the first column more completely. As will be shown in a later section in which two different ion-exchange resins are compared, different resin samples gave markedly different exchange capacities (even fresh, unused resin samples) ranging from 8.8 to 20 g of sodium dichromate per 100 ml of the resin. The consequence of this variation in exchange capacity is to increase or decrease the time interval between successive regenerations depending upon which resin is in use during the treatment cycle.

RESIN LIFE

Our next endeavor was to make some estimate or projection of resin life. Resin suppliers were pessimistic and were predicting as much as one-third mortality of the resin each year if we exposed it to 2700 ppm dichromate at a low pH. As will be shown later, our experience is not nearly that bad, and is closer to a 15% replacement over a two year period.

From the literature the Rohm & Haas "macroreticular" resin with a "stronger backbone" appeared to offer the best chances for success.[9]

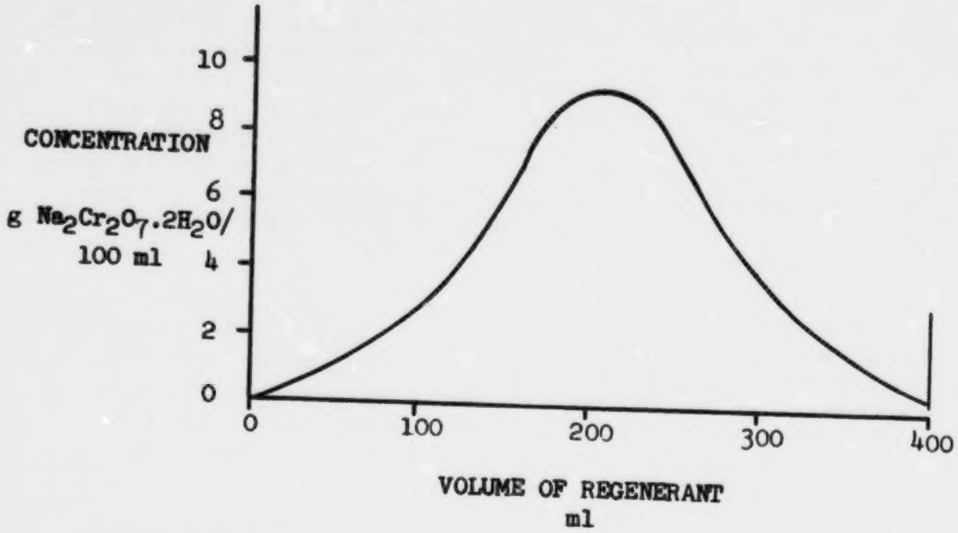


FIGURE 1 TYPICAL CURVE OF CONCENTRATION OF DICHROMATE IN REGENERANT VERSUS VOLUME FOR ONE PASS.

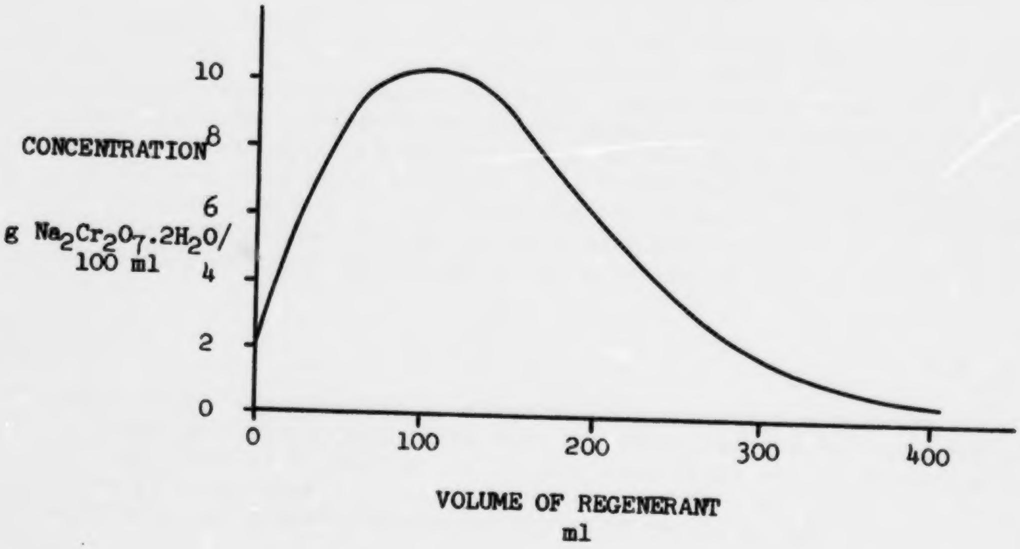


FIGURE 2 TYPICAL CURVE OF CONCENTRATION OF DICHROMATE IN REGENERANT VERSUS VOLUME WHEN THE INITIAL VOLUME IS RECYCLED.

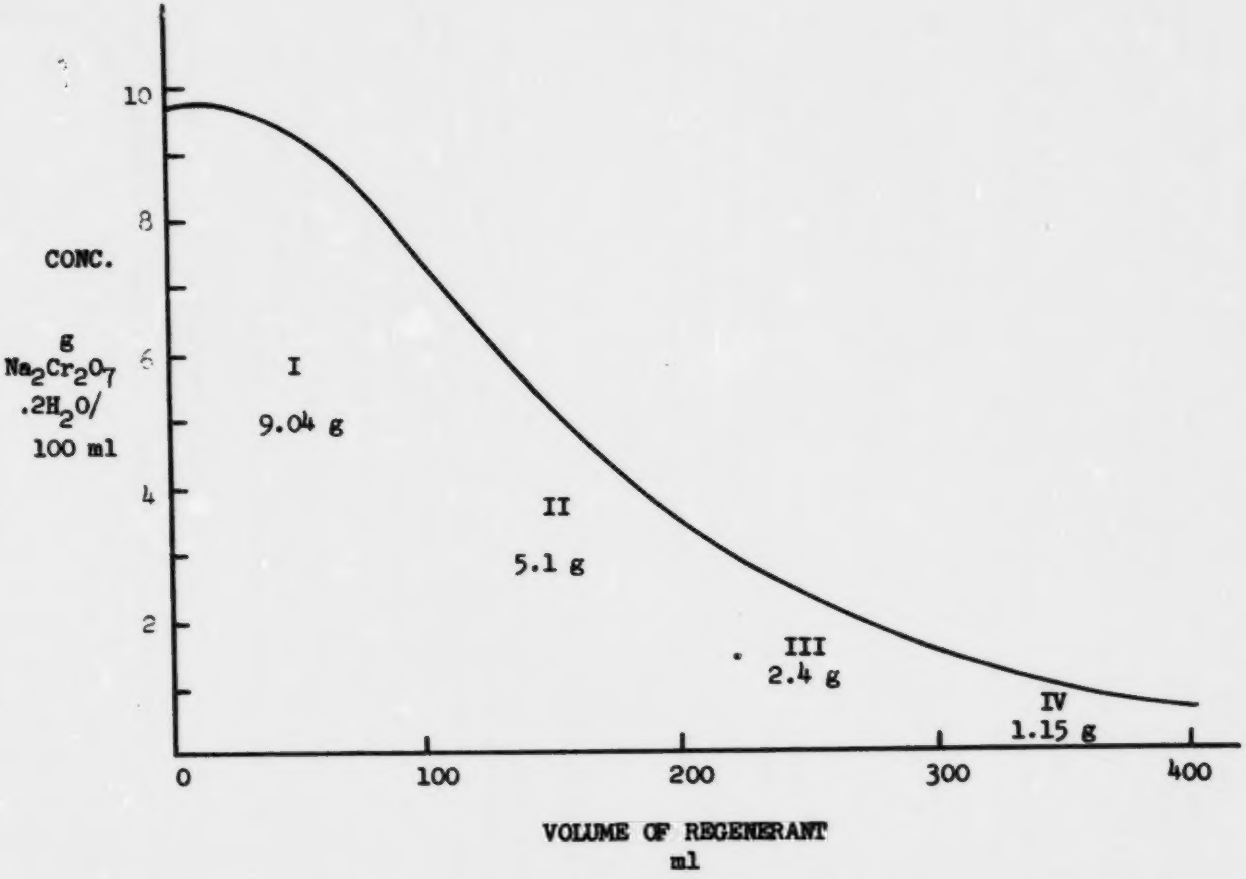


FIGURE 3 PLOT OF CONCENTRATION VERSUS VOLUME FOR A REGENERATION IN WHICH PORTIONS III AND IV FROM THE PREVIOUS REGENERATION WERE RE-USED AS PORTIONS I AND II

During eight months of testing the Nalco (Dow) resin was tested for twenty-six cycles, and the Rohm & Haas resin for sixty-five cycles of exhaustion and regeneration. Figure 4 is a plot of grams of sodium dichromate per "100 ml" of resin versus cycles or time. The 100 ml is in quotes because it was discovered after a period of time (26 to 37 cycles) when the volume was remeasured that we had only from 81.5 to 96.0 ml of resin remaining in each of four resin columns. Part of this discrepancy was from mechanical loss (i.e., carrying the resin beads out of the column during backwash. These beads were visible in the retained backwash liquors.) and part of it is probably the result of a predicted resin breakdown by contact with the relatively high concentrations of chromium (VI) solution at low pH.

If the volume of resin lost is replaced (or if the capacity is calculated on the basis of the actual volume present) the resin retains essentially its original capacity for chromium.

Throughout this report exchange capacities will be expressed in terms of the volume of ion exchange resin present, that is, as the weight, in grams, of sodium dichromate which is adsorbed on 100 ml of resin, or, in the plant operation, as pounds per cubic foot. It should be pointed out, however, that this volume is not a very precise parameter, first, because the resin particles are small spheres and a given mass may occupy a greater or lesser volume depending upon how closely packed the spheres are, one to the other. Also, the volume changes by as much as 20% depending on whether the resin is completely regenerated (in the chloride salt form) or completely exhausted (in the dichromate, or polychromate salt form.)

THE ION-EXCHANGE RESIN

There are a number of suppliers of ion-exchange resins. We began our laboratory study with two and have, arbitrarily, limited our study to a comparison of these two; Dow Chemical's Dowex 1X8 and Rohm and Haas' Amberlite IRA-900C. These are both strongly basic anion exchange resins. They are polymers of styrene, cross-linked with divinyl benzene and their functional groups are quarternary ammonium groups.[9,10]

The Dowex 1X8 was reportedly the "SBR" resin used by Nalco Chemical Company in their Patent 3,223,620 and which was shown by them to have a specificity for dichromate over many other anions.

The Rohm and Haas Amberlite IRA-900C is a macroreticular (or sponge-like) resin with larger pores and a stronger "backbone", which is advertised to be less prone to mechanical breakdown. Mechanical breakdown results in an accumulation of fine particles which yield a high pressure drop across the resin bed, and a loss of exchange capacity.

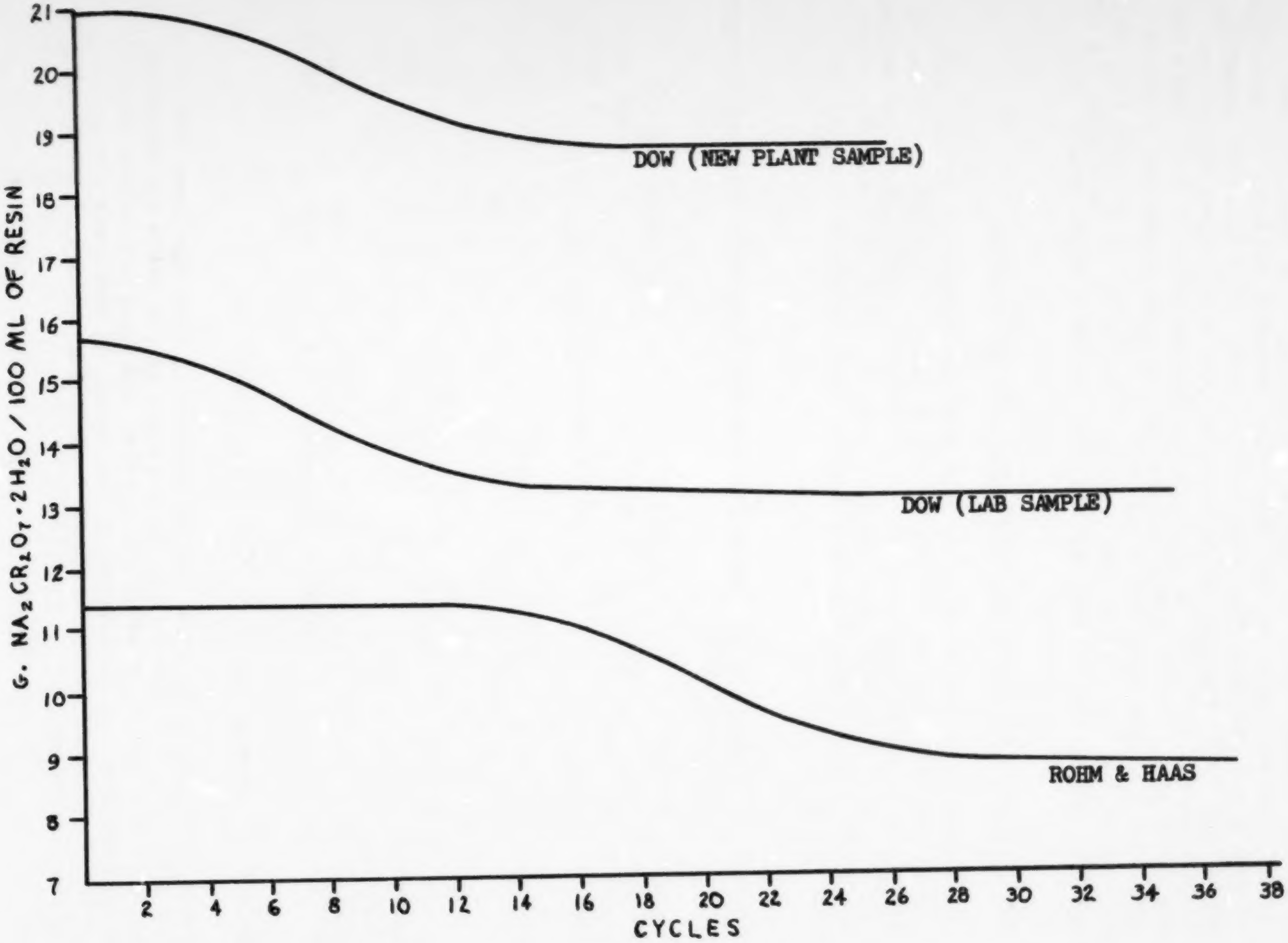


Figure 4 CURVES SHOWING THE CHANGE IN EXCHANGE CAPACITY WITH TIME

From our initial laboratory tests it was apparent that there were advantages and disadvantages to both of the resins. The Dowex 1X8 had a larger capacity, however, the beads were somewhat gellular and more prone to mechanical damage. The Amberlite IRA-900C, with its lower capacity, would have to be regenerated more frequently in our plant operation, (approximately every 14 to 18 hours as compared with 20 to 24 hours for the Dowex 1X8,) but it appeared to regenerate and rinse with a little less care and time than the Dowex 1X8. We elected to continue our comparison of the two resins into the plant operation by installing the Dow resin in one of the columns and the Rohm and Haas resin in the other.

THE CAPACITY OF THE ION-EXCHANGE RESINS FOR DICHROMATE

In Table 2 we have recorded the data from our estimation of the capacity of four different resin samples to adsorb sodium dichromate. It can be seen from this table that there is considerable variation in the exchange capacity of the resin from sample to sample. Also, the capacity of the Dow resin is significantly greater than the capacity of the Rohm and Haas resin.

Table 2 ESTIMATION OF DICHROMATE EXCHANGE CAPACITIES FOR FOUR DIFFERENT RESIN SAMPLES

Resin Identity	IRA-900C		Dowex 1X8	
Sample Source	Lab	Plant Stock	Lab	Plant Stock
Resin Volume (ml)	81.5	96.0	89.0	93.0
Cycle	grams of $Na_2Cr_2O_7 \cdot 2H_2O$ adsorbed			
1	8.84	12.07	13.94	18.19
2	9.18	12.56	12.92	17.85
3	9.86	11.73	12.58	19.38
4	9.18	11.90	12.92	19.04
5	9.18	11.73	12.92	19.21
Average	9.25	12.00	13.06	18.73
Capacity				
g/100 ml	11.35	12.50	14.67	20.14
lbs/cu ft	7.08	7..80	9.16	12.57

EFFECT OF INFLUENT pH

The conclusions drawn from this work were; 1) that the lower the pH of the influent, the greater was the capacity of the resin for chromium, 2) the lower the influent pH the greater the permissible flow rate to obtain satisfactory adsorption by the resin, 3) the lower the influent pH the lower would be the chromate content (the color) of the total averaged effluent.

Table 3 PRELIMINARY DATA ON THE EFFECT OF INFLUENT pH

Influent pH	Volume of influent ml	Flow rate ml/min	Color of Averaged Effluent Taylor Scale
1.10	1500	335	<100
2.00	1500	382	<100
2.80	1000	201	>200 <300
3.00	1000	160	>200 <300
3.10	1000	143	>300
3.40	1000	145	>300
3.80	1000	143	>400

Most of the laboratory work which immediately followed the above study was done with an influent pH of 2.0 or 2.5. Later, as we began to specify materials of construction for the plant, this low pH of the influent presented problems. Together with the high sodium chloride content, the low pH ruled out the use of stainless steel. Most of the available flow meters, filters and multi-port valves were not available in materials which would withstand the low pH, high cloride exposure as well as the high pH of the alkaline regenerant solutions. We extended this study with more tests to evaluate the effect of the influent pH and obtained the results as shown in Table 4-6.

From this latter series of tests we concluded that a satisfactory resin performance could be obtained with an influent pH of 3.0 and only when the pH of the influent approached 4.0 did the capacity at bleed (the point where secondary treatment becomes necessary), the quantity of dichromate required to exhaust a column and the concentration of the recovered regenerant solutions begin to decrease significantly. From these findings we were then able to specify stainless steel as satisfactory for many of the contact surfaces in the final plant design.

Table 4 EFFECT OF INFLUENT pH ON THE CAPACITY OF THE ION-EXCHANGE RESINS TO THE POINT WHERE BLEEDING OCCURS

Resin Identity	IRA-900C	Dowex 1X8
Influent pH	Average Capacity At Bleed grams $Na_2Cr_2O_7 \cdot 2H_2O$/100 ml of resin	
2.5	9.72	19.56
3.0	9.21	19.65
3.5	10.09	18.46
4.0	8.85	18.28

Table 5 EFFECT OF INFLUENT pH ON THE CAPACITY OF THE ION-EXCHANGE RESINS AT EXHAUSTION

Resin Identity	IRA-900C	Dowex 1X8
Influent pH	Average Capacity At Exhaustion grams $Na_2Cr_2O_7.2H_2O$/100 ml of resin	
2.5	12.50	20.13
3.0	12.66	21.57
3.5	12.66	21.12
4.0	11.69	19.92

Table 6 EFFECT OF INFLUENT pH ON THE CONCENTRATION OF DICHROMATE IN THE RECOVERED REGENERANT SOLUTIONS

Resin Identity	IRA-900C	Dowex 1X8
Influent pH	Concentration of Combined Portions I and II Of The Recovered Regenerant Solutions grams of $Na_2Cr_2O_7.2H_2O$/100 ml of solution	
2.5	5.85	8.75
3.0	6.08	8.84
3.5	5.63	8.71
4.0	5.27	8.21

CONCENTRATION OF DICHROMATE IN THE INFLUENT

Samples of the untreated zinc yellow plant effluent were acidulated to an appropriate pH value and analyzed iodometrically for total chromium(VI). The results of some of these analyses are reported in the second column of Table 7. Generally the concentrations, expressed as parts of sodium dichromate dihydrate per million, vary between 1600 and 2700 ppm. The variations are due in part to variations in the properties of the zinc oxide which is used in the pigment manufacture. Variations are also due to failure of the product recovery filters to consistently function properly to remove all of the suspended pigment from the filtrate. The reading of 11,000 ppm reported on line 3 of column 2 in the table was the result of such an abnormal loss.

THE VOLUME OF INFLUENT AND THE QUANTITY OF DICHROMATE REQUIRED TO CAUSE A COLUMN TO BLEED

In our laboratory evaluation of the ion-exchange resins we recorded the volume and the dichromate concentration of the influent which was required to cause a 100 ml resin column to "bleed" the yellow dichromate color. During our earliest work little attention was paid to a faint yellow coloration in the effluent from the column. Later, when we were insisting on a water-white, "dichromate-free" effluent, the first visible coloration was recorded as the "bleed" volume. This is the point at which secondary treatment, or treatment through a second resin column in series would be required.

Table 7 THE INFLUENT CONCENTRATION, THE VOLUME OF INFLUENT AND THE QUANTITY OF DICHROMATE REQUIRED TO CAUSE A 100 ml RESIN COLUMN TO BLEED

Sample Number	ppm $Na_2Cr_2O_7.2H_2O$ In The Influent	Volume To Bleed	Weight Of $Na_2Cr_2O_7.2H_2O$
1	2210	6000	13.26
2	2300	5400	12.42
3	11,000	900	9.90
4	1600	6000	9.60
5	2000	6000	12.00
6	1900	4800	9.12
7	1900	5400	10.26
8	1600	7800	12.48
9	1600	5600	8.96
10	2700	4400	11.88
11	1500	7200	10.80
12	2000	6200	12.40
13	2100	6600	13.86
14	1900	6000	11.40
15	1700	6200	10.54
16	1900	6100	11.59
Average	1927*	5980	11.28

* This average was determined omitting the 11,000 ppm reading.

The volume of influent of a corresponding concentration which is required to cause a bleed is reported in column 3 of Table 7. As might be predicted, when the concentration is high, the volume to bleed is low and vice versa. Because of the variation in influent concentration, one could not expect, for instance, to run a fixed volume of influent through the column and then initiate secondary treatment. To do so would result in other than a satisfactory or optimum performance.

The quantity of sodium dichromate in grams required to cause a 100 ml resin column to bleed is reported in column 4 of Table 7. This value is somewhat more reproducible than the volume to bleed.

THE VOLUME OF INFLUENT AND THE QUANTITY OF DICHROMATE REQUIRED TO EXHAUST A RESIN COLUMN

Similar to the above study we observed the volume of influent and the quantity of dichromate required to "exhaust" each resin column. This "exhaust" point was even more subjective because it was determined visually by comparing the color intensities of the influent and the effluent from the column. Representative values are reported in Table 8.

Table 8 THE VOLUME OF INFLUENT AND THE QUANTITY OF DICHROMATE REQUIRED TO EXHAUST A 100 ml RESIN COLUMN

Sample Number	ppm $Na_2Cr_2O_7.2H_2O$ In The Influent	Volume To Exhaust	Weight Of $Na_2Cr_2O_7.2H_2O$
1	2210	7200	15.91
2	2300	8500	19.55
3	11,000	1400	15.40
4	1600	7900	12.64
5	2000	7400	14.80
6	1900	7500	14.25
7	1900	9200	17.48
8	1600	10,300	16.48
9	1600	7200	11.52
10	2700	6300	17.01
11	1500	10,700	16.05
12	2000	9400	18.80
13	2100	8200	17.22
14	1900	7900	15.01
15	1700	8300	14.11
16	1900	8200	15.58
Average	1927*	8280	15.74

* This average was determined omitting the 11,000 ppm reading.

CONCENTRATION OF DICHROMATE IN THE RECOVERED REGENERANT

After considerable study of the regeneration process we adopted a procedure in the laboratory of using four 100 ml portions of regenerant solution to regenerate a column which contained 100 ml of the ion-exchange resin. The first two portions of regenerant which contained the highest concentrations of dichromate would be recycled to manufacturing. Portions three and four from one regeneration would become portions one and two respectively for the next regeneration. Each portion of regenerant was analyzed for its chromium content. Typical results of this work are listed in Tables 12, 13, and 14 of Appendix B.

From 16 such cycles with the Rohm and Haas resin the average composition of the first portion was 6.71 g of sodium dichromate per 100 ml and for the second portion 4.14 g per 100 ml. Since in the plant we will be combining portions one and two, we can expect an average composition of 5.43 g per 100 ml from regeneration of the IRA-900C resin.

Similarly, from the original laboratory sample of the Dow resin we obtained a dichromate concentration of 9.14 g/100 ml for the first portion of regenerant, 5.45 g/100 ml for the second portion and the two portions combined can be expected to give a concentration of 7.30 g/100 ml.

A sample of Dow resin taken from the plant stock gave somewhat higher results, namely 10.67 g/100 ml, 6.73 g/100 ml and an average composition of 8.70 g of sodium dichromate per 100 ml. We will be comparing these values with those obtained in our plant operating experience later in the report.

AN ACCOUNTING FOR THE DICHROMATE INTRODUCED IN THE INFLUENT

Inasmuch as all of the dichromate which was introduced to a given column was picked up either by that column or by the second column in series, no dichromate should be lost from the laboratory system. All dichromate in the influent should be accountable either in the regenerant, in the rinse water or in the back-wash water. Again, since regenerant portions three and four from a given regeneration become portions one and two for the next regeneration cycle we must concern ourselves with the increase in dichromate content in these re-used portions, not with their total dichromate content. In Appendix B we have given the details of this study and in Table 17 we have accounted for the total dichromate content in the influent, the final less the initial dichromate content of regenerant portions one and two, and the dichromate content of portions three and four, the rinse water and the back-wash water for 58 such laboratory cycles. From this study we succeeded in accounting for 99.5% of the influent dichromate.

SCALE-UP

Following the laboratory evaluation and the decision to proceed with the plant design and construction, it was necessary to determine a number of parameters for scale-up.

On completion of the laboratory determination of the resin capacity and the rate of chromate loss in the pigment waste water, it was necessary to decide how long it would take to regenerate, or how frequently we wished to regenerate. We elected to regenerate no more frequently than every twelve hours, both to decrease the amount of laboratory analytical work and to make the regeneration coincide with our manufacturing schedule. This determined the size of the resin columns, the size of the regenerant tanks, and ultimately the sizes of the pipes, pumps, flow meters, and filters.

Another requirement was to determine the rate at which concentrated hydrochloric acid would have to be added to the influent to maintain a pH of 3.0 and the amount of 20% (weight/volume) sodium carbonate solution which would be required to continuously adjust the effluent pH to 9.0[11] to precipitate the remaining zinc ions so that they could be removed by filtration before the waste water was finally discharged to a nearby surface stream.

Other requirements were the length of the light path necessary to colorimetrically detect one ppm of chromium present as the dichromate ion and the size of the heat exchanger necessary to raise the regenerant temperature to 50°C at a rate of 50 gal/min to the resin column.

PLANT DESIGN

GENERAL CRITERIA

There were a number of factors which influenced the design of the treatment plant. Among these were:

1. The exchange of anions is an equilibrium process. At any cross-section in the tower during treatment there is an equilibrium between the dichromate and chloride concentrations adsorbed on the resin and the dichromate and chloride ion concentrations present in the water solution. As the solution passes downward to a lower level in the column it contacts resin which contains a lesser concentration of adsorbed dichromate and conditions are again favorable for a further exchange. Here the resin again adsorbs an additional quantity of dichromate from the waste water and gives up to the solution an equivalent quantity of chloride ion.

2. Exhaustion or saturation of the resin is accompanied by a twenty percent decrease in the resin volume and a corresponding increase in the particle density. During backwash or when the resin is suspended in the regenerant solution these more dense, exhausted resin beads fall to the bottom of the column. This is the main argument for up-flow regeneration. In our experience, up-flow regeneration is only successful when the flow is completely uniform over the entire floor of the resin column. If there are any areas not subject to up-flow, these areas tend to collect the exhausted (most dense) resin, and the end result is an incomplete regeneration. An incomplete regeneration results in the inability to obtain a chromium-free water-white effluent on the next use of that column.

3. Pressures of three to seven psig are required to drive a liquid through a four foot deep compact resin bed at reasonable flow rate. (1 to 3 gal/cu ft/min[12]) For this reason the resin columns and the column covers must be capable of withstanding these pressures and pumps must be capable of overcoming these back-pressures at the required flow rates.

4. The density of the regenerant solution is considerably greater than the density of water. Another problem with up-flow regeneration occurs when one attempts to displace the last portion of

regenerant solution by pumping water upward from below. The less dense water tends to channel unevenly upward through the resin bed and results in an undue dilution or an incomplete removal of the alkaline regenerant solution. Removal by down-flow results in an undesirable re-exchange between the most thoroughly regenerated resin at the bottom of the tower and the chromate-containing regenerant which had previously passed through the column during the latter stages of the up-flow regeneration.

5. In order to obtain a dichromate-free, water-white effluent, the regeneration of the resin must be complete and uniform. As indicated in paragraphs 1. through 4. above, this is an equilibrium process and the resin containing adsorbed dichromate is more dense tending to settle at the bottom of the column. Also it is necessary to back-wash the resin bed thoroughly to prevent channeling or a compaction of the resin beads with an accompanying pressure drop once the system is returned to the treatment mode. If, following an incomplete regeneration, the resin bed is back-washed, the most exhausted resin beads are at the bottom of the resin column in contact with the column effluent. Even if the solution being treated is water-white above this point, it will, as it passes the incompletely regenerated resin beads at the tank bottom, redissolve dichromate from the resin and the chromium content of the column effluent will be above statutory limits.

6. To accomplish such a complete regeneration, flow through the resin bed must be uniformly distributed. Considerable attention to the design of both the top and bottom diffuser assemblies was necessary in order to prevent dead areas, bed inversions and channeling along the side walls of the resin columns.

7. Regeneration proceeds more rapidly at elevated temperatures, but the ion-exchange resin is more vulnerable to oxidative attack at higher temperature[13]. Since the regenerant storage tanks were not insulated rather than maintain the temperature of the regenerant solutions at 45° to 50°C continuously, we elected to pass the regenerant through a heat exchanger on its way to the column to be regenerated. Our data on resin life was obtained utilizing a regeneration temperature of 45° to 50°C and we have concluded that this temperature is high enough to allow regeneration in a reasonable time and not so high as to place the resin in jeopardy because of thermal or oxidative attack.

8. The resin is also more vulnerable to attack and decomposition when it is in the free base (hydroxyl) form than when it is in the salt (chloride) form. While the original plant design had a provision for the gradual re-introduction of sodium hydroxide to the regenerant as the base was utilized by the acidic dichromate; this was unnecessary. Again, our resin life statistics which have been developed over two years were determined using a regenerant in which

the required quantity of the sodium hydroxide was added initially. This actually resulted in a further cost saving, inasmuch as any additional base added had to be re-neutralized with acid before the recovered chromate solution could be used in manufacturing the zinc yellow pigment. The raw material required in zinc yellow manufacture is sodium or potassium dichromate, not sodium chromate.

9. Salt solutions can easily be made with a density of 1.14 (approximately 21% weight by weight KCl), sufficient to float the resin beads. When floated, the resin can be pumped with a diaphragm pump without any significant damage to the resin beads. This technique is utilized whenever it is necessary to replace the screens in the bottom diffuser, or to make repairs to the diffuser or to the tank coating.[14]

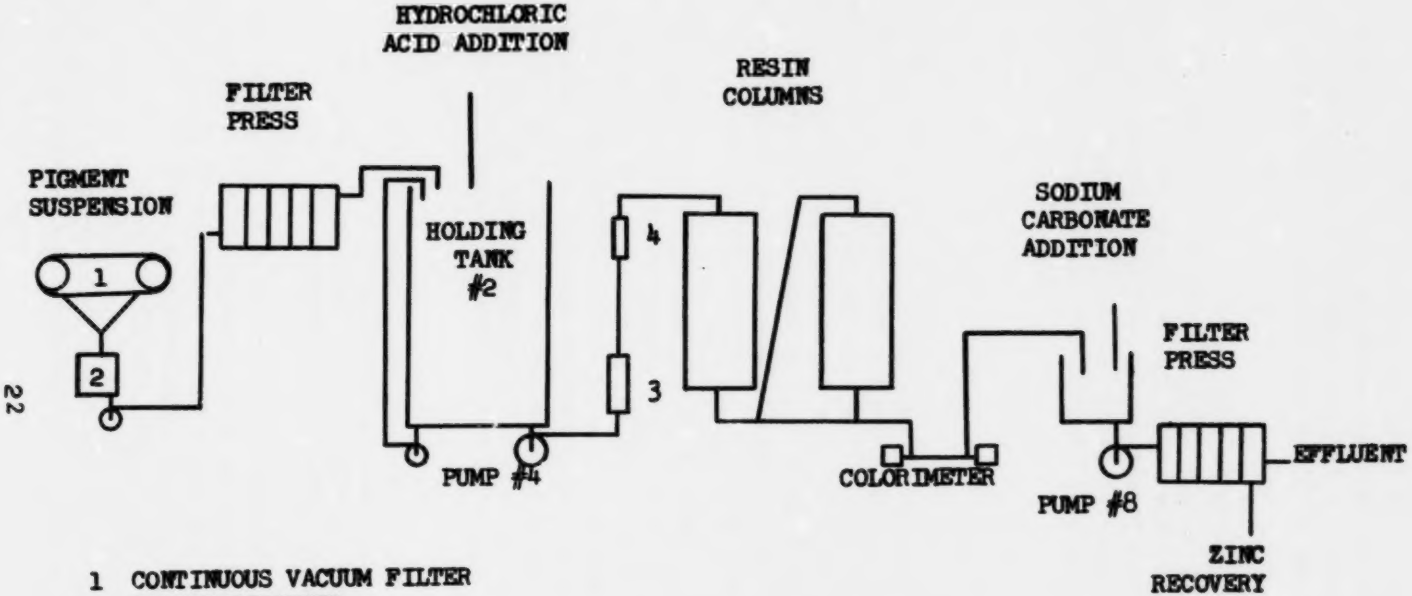
TREATMENT FLOW

The treatment flow as depicted by equation (5) is illustrated in Figure 5. Filtrate and wash liquors from a continuous vacuum filter are recovered in a vacuum receiver. They are pumped through a filter press which removes most of the solid lost in the initial filtration process and then they are collected in a holding tank. In the holding tank hydrochloric acid is added continuously to adjust the pH to 3.0, the desired treatment pH value.

The acidified waste water is then pumped through a sock-type filter to remove any foreign matter which might accumulate in the ion-exchange resin bed, and then through a flow meter to the resin columns. Initially, passage through a single column is sufficient to remove all of the dichromate. As this first column adsorbs more and more dichromate a low concentration will begin to bleed from the resin bed. This bleeding is picked up in what is called "Secondary Treat" by causing the waste water to flow through a second column, in series, prior to discharge.

All of the effluent from the resin columns passes through the colorimeter and its color is continuously recorded on a strip chart. From the colorimeter the water solution passes to a small, well agitated tank where sodium carbonate solution is added to pH 9.0.

When the pH of the ion-exchange column effluent is raised to 9.0 the zinc ions precipitate as a mixed zinc hydroxide-zinc carbonate. This white solid is filtered from the effluent solution in plate-and-frame filter presses. The filter cake is washed with water to remove adhering sodium chloride and then dried. The dried powder contains 70 to 72% ZnO. With the present shortage of zinc oxide the prospects are good that we will develop a market for this by-product solid to a user interested in its zinc content. It does contain low level concentrations


HYDROCHLORIC ACID ADDITION
FILTER PRESS
RESIN COLUMNS
PIGMENT SUSPENSION
1
HOLDING TANK #2
4
SODIUM CARBONATE ADDITION
FILTER PRESS
2
3
PUMP #4
COLORIMETER
PUMP #8
EFFLUENT
ZINC RECOVERY

1 CONTINUOUS VACUUM FILTER
2 VACUUM RECEIVER
3 SOCK FILTER
4 FLOW METER

FIGURE 5 ILLUSTRATION OF THE TREATMENT SYSTEM

of iron and silica and occasionally chromium (III) as contaminants.

As indicated in the introduction, with satisfactory regeneration of the ion-exchange resin we can be assured of an effluent which contains less than 1.0 ppm of chromium. In the event it becomes necessary to attain a specification of 0.05 ppm of hexavelent chromium some post treatment will be required at this point.

THE ELECTROMECHANICAL CONTROL OF THE TREATMENT SYSTEM

The various functions which are involved with the treatment of the dichromate-containing influent with the ion exchange resin and the subsequent regeneration of the ion exchange resin are controlled through one master electromechanical logic system. For control purposes the circuiting is divided into a treatment system and a regeneration system. The two systems are electrically interlocked such that a column which is being regenerated cannot be called upon for treatment or secondary treatment and vice versa. With the exception of a few common alarms, the two systems operate essentially independently.

The entire system was devised so that the operator could control the timing, and to some extent the sequence of events, manually, or the system could be called upon to follow the programmed sequence of events automatically. The system was further designed to include a number of safety interlocks so that an operator could not, for instance, attempt to pump liquid to an already filled tank, or attempt to regenerate without first making up the regenerant solutions by appropriate additions of caustic soda and potassium chloride to the make-up water.

Treatment is initiated, first, by making a selection for manual or automatic operation and then by selecting the tank which is to be used for treatment. Depressing the appropriate "Treat" button on the control panel; 1) activates the colorimeter and the influent and effluent pH control loops (which will be discussed more fully in later sections.) 2) starts the influent feed pump and the level actuated pump on the zinc precipitation tank (Tank 911 in Figure 11) 3) positions the main multiport valves to direct the influent through the chosen resin column and through the colorimeter to the zinc precipitation tank. The operator is called upon to adjust the flow to the column with a manually operated valve. He adjusts the set points on the colorimeter, cleans and maintains the influent sock filters and maintains the quantity of acid in the storage tank for the influent pH adjustment and of sodium carbonate solution in the storage tank as required for the effluent pH adjustment and zinc precipitation.

Secondary treatment, which again can be called for manually or automatically, is initiated when a yellow dichromate color begins to bleed from the resin column which is being used for treatment. If the second resin column has been regenerated and is ready for use, on secondary treat, the

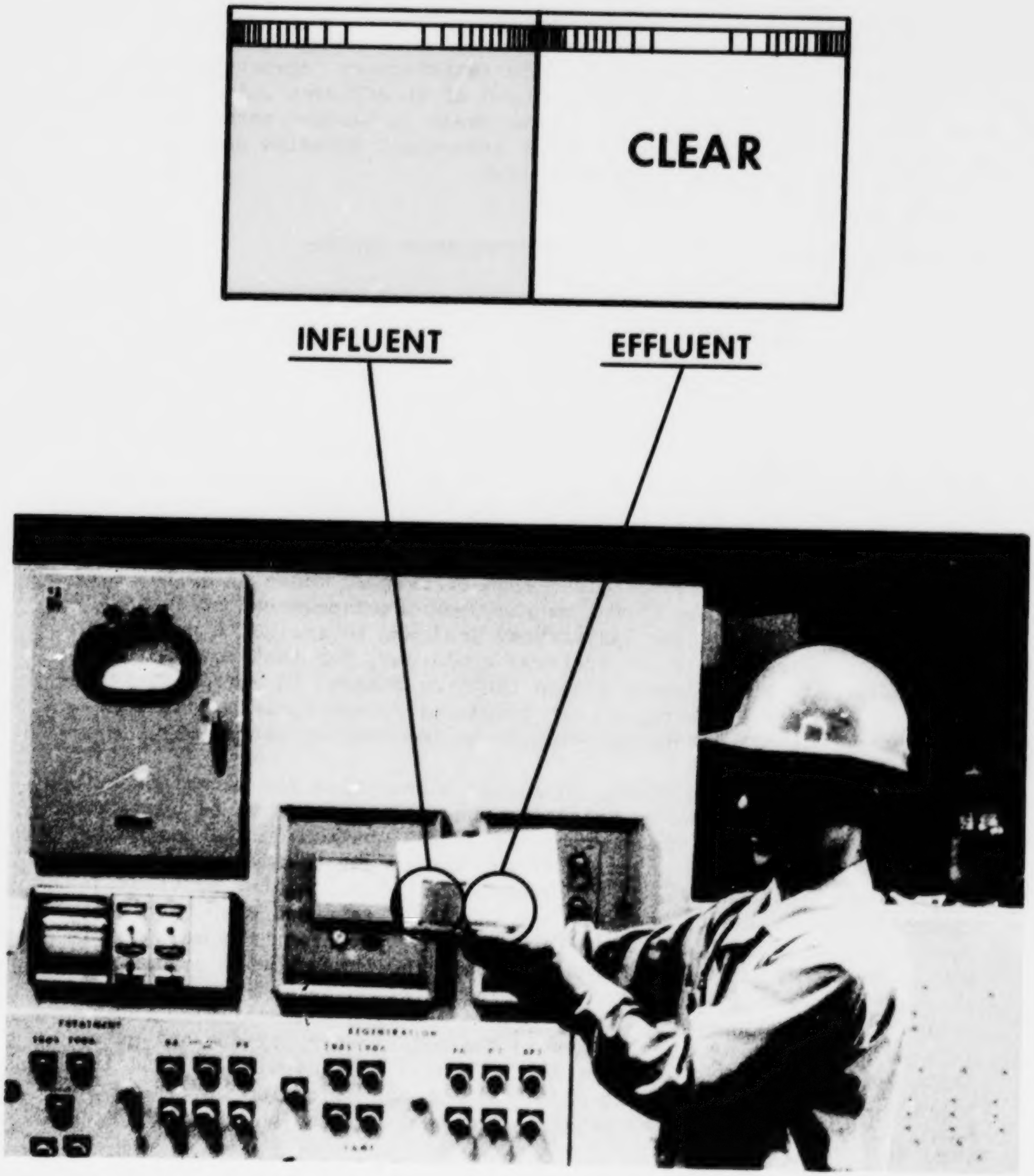

CLEAR
INFLUENT
EFFLUENT

Figure 6 ILLUSTRATION OF THE COMPARISON BETWEEN THE SYSTEM INFLUENT AND THE CLEAR EFFLUENT

main multiportvalves will now be oriented so that the flow from the column which is bleeding will be directed to the inlet of the fresh column. The effluent from the latter column is directed through the colorimeter to the zinc precipitation tank for pH adjustment. In the event that the second resin column is not ready for use, the treatment system will sound an alarm, display an appropriate light on the panel alarm board and shut down.

REGENERATION FLOW

Regeneration flow as represented by equation (6) is illustrated in Figure (6). When a resin column is saturated with dichromate, usually 2 to 4 hours after the initiation of secondary treat, the system proceeds to regenerate this saturated, or exhausted, resin column.

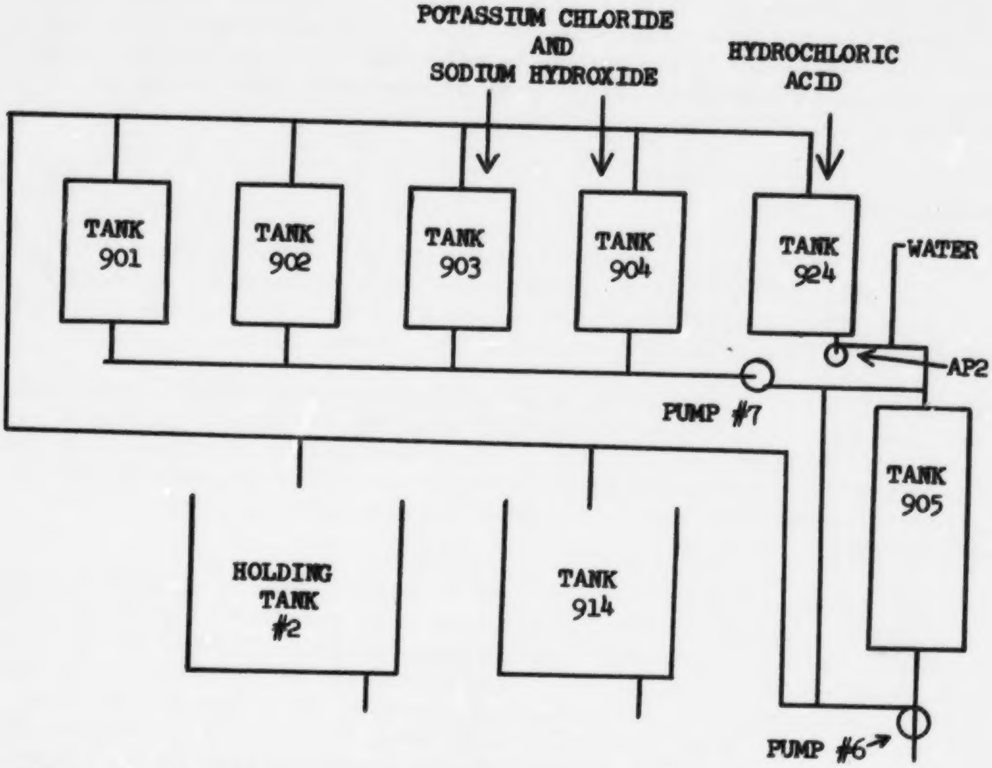
Wash water is introduced in order to limit the amount of zinc ion which might precipitate on the resin surface when the alkaline regenerant solution is later added. A visibly low concentration of chromate in the rinse water has usually proved satisfactory. That is, removal of dichromate ion is also indicative that the accompanying zinc ion has been removed.

The resin column is completely drained to avoid dilution of the regenerant solution. The alkaline salt solution from the first regenerant holding tank (Tank 901 in Figure 7) is pumped through the bottom of the column to displace air from the bed and to begin the neutralization of the acid dichromate which is adsorbed on the resin. When contact is made with the top level probe in the resin column, the flow is reversed. The regenerant is recycled through the bed for a brief period (3 to 5 minutes), then it is pumped to the chromate recovery tank (Tank 914 in Figure 7). When the level in Tank 901 falls below the bottom level probe in this tank, the valve beneath Tank 901 closes and the valve under Tank 902 opens.

Four portions of regenerant are pumped in this manner through the resin bed. The first two which will be highest in chromate content are pumped to Tank 914 where they are re-acidified to the dichromate pH, analyzed for chromium and potassium content and eventually used in the preparation of a succeeding batch of zinc yellow pigment. The second two regenerant portions are used to refill Tanks 901 and 902 and will be used as the primary regenerant of the next regeneration cycle.

Water is then flowed through the resin bed to remove adhering regenerant and this water is used to refill Tanks 903 and 904. Rinsing is continued until the rinse pH drops below the value of 10. This value was obtained simply by observation. The excess rinse water is returned to the holding tank (Tank 2) where it will be recycled into treatment.

A dilute hydrochloric acid solution is then pumped through the resin column to acidify the column and prepare the resin surface for the next


POTASSIUM CHLORIDE
AND
SODIUM HYDROXIDE
HYDROCHLORIC
ACID
TANK
901
TANK
902
TANK
903
TANK
904
TANK
924
WATER
AP2
PUMP #7
TANK
905
HOLDING
TANK
#2
TANK
914
PUMP #6

TANK 2	IS THE INFLUENT HOLDING TANK
TANKS 901	THROUGH 904 ARE USED FOR THE ALKALINE REGENERANT SOLUTION
TANK 905	IS ONE OF TWO ION-EXCHANGE RESIN COLUMNS
TANK 914	IS THE HOLDING TANK FOR THE RECOVERED CHROMATE SOLUTION
TANK 924	IS USED FOR DILUTE ACID STORAGE
AP2	IS AN ACID PUMP
PUMP #6	IS USED TO PUMP REGENERANT TO THE RESIN COLUMNS
PUMP #7	IS USED TO PUMP REGENERANT AND RINSE SOLUTIONS FROM THE RESIN COLUMN TO STORAGE OR RECYCLE

FIGURE 7 ILLUSTRATION OF THE REGENERATION SYSTEM

treatment cycle. The hydrochloric acid solution of necessity by-passes the stainless steel regenerant flow meter.

Potassium chloride and sodium hydroxide are added by the system operator to Tanks 903 and 904 to prepare these solutions for the next regeneration cycle.

THE ELECTROMECHANICAL CONTROL OF THE REGENERATION SYSTEM

The regeneration system controls the sequence of all of the events which must occur in order to recover the dichromate for re-use and to renew the resin for a future treatment cycle. It is somewhat more complex than the treatment system. Physically it is simply to: 1) drain and wash the spent resin, 2) pump two portions of regenerant from storage tanks through the resin solumn to a holding tank for re-use, 3) pump two additional portions of regenerant from the make-up tanks through the resin column to the intermediate storage tanks, 4) wash the column free of regenerant, 5) reacidify the column and re-fill it with water until it is required for a future treatment cycle. The events are physically connected, i.e., the volume from one tank which is being emptied is used to re-fill a second, and this is used to advantage in the sequencing scheme.

The heart of the regeneration control system consists of three sequencing relays as illustrated in Figure 8. One controls in which direction a regenerant liquor shall be pumped through the resin column (i.e., upflow or downflow). The second relay controls from where the regenerant liquor is being pumped and the third relay controls to where the regenerant liquor will be pumped. Each contact position on each of these sequencing relays operates another relay which, in turn, activates the proper pumps, valve actuators, level controls, timers, etc., which are necessary to perform the particular function or combination of functions called for. The sequencing relay is advanced to its next position by an electrical pulse signal generated by a device which senses the completion of the previous step. For example, the second sequencing relay will first open the valve beneath the first regenerant storage tank (Tank 901 in Figure 7) and allow the tank contents to flow to the pump for transfer to the resin column until a level probe at the bottom of Tank 901 loses contact with the liquid. This loss of contact will close a relay to indicate to the system that Tank 901 is empty and advance the second sequencing relay to its next position. This next position will open the valve beneath Tank 902 for its contents to be used in regeneration. When Tank 902 is emptied Tank 903 will be tapped, etc. During this time the flow from the resin column is being directed to the holding tank for re-use (Tank 914 in Figure 7) by the proper positioning of the third sequencing relay. When Tank 914 is full a level control advances the third sequencing relay to direct the flow to re-fill Tank 901. This type of process continues throughout the regeneration until the sequencing relays have all returned to their original positions, indicating the completion of regeneration.

The last position on the first sequencing relay turns the regeneration system off. In addition to using level probe relays to signal the completion of a particular step in the sequence, adjustable timers are also used to generate the relay advance pulse. Relays connected to the pH sensing system are used to signify when the resin has been satisfactorily rinsed to remove the alkaline regenerant and when it has been properly acidulated at the end of regeneration. Built within this framework are all of the process function controls, alarms and interlocks required for satisfactory operation.

FILTRATION

The resin beds would act as filters to collect and accumulate any foreign matter present in suspension in the influent. To avoid this accumulation sock filters are installed in the treatment and in the regeneration pipelines ahead of the flow meters. These filters are arranged to back-wash themselves every 30 minutes, or the operator can manually initiate back-wash in the event the flow drops below 30 gallons per minute. Filtered water from the parallel sock filter is down-flowed through the blinded sock from the inside and, thus, releases most of the accumulation. This small quantity of water is directed to the plant's reduction-precipitation process for waste disposal, where the slight amount of foreign matter presents no disposal problem. The arrangement of the filters is shown in Figure 9.

pH CONTROL

There are three pH monitors and two pH control loops in the chromate recovery system.

The first loop is shown in Figure 10. A sample stream from Tank 2 is directed through the pH flow-cell and returned to Tank 2. The output signal from this pH amplifier is directed in series through high and low pH alarms, the controller of a precision chemical pump, and a signal receiver which in this case is a pH recorder.

The pH in Tank 2 is monitored and controlled at the value 3.0. If the pH in Tank 2 falls below 3.0 the signal amplifier, with proportional control, causes the acid pump AP1 to decrease its stroke and deliver a smaller quantity of acid to Tank 2.

Pump 4, the cartridge filters, and the flow meter are all fabricated in 316 stainless steel, and must be protected against low pH (and high chloride ion) exposure. In the event the pH falls below 2.2, the low pH alarm will sound until answered by the system operator.

Zinc yellow pigment, which would be in suspension in the filtrate and wash liquors as they enter Tank 2 at a pH of about 6.3, will dissolve completely at a pH of 3.0. If the pH in Tank 2 is permitted to rise above 3.0, conditions for adsorption of dichromate by the ion-exchange

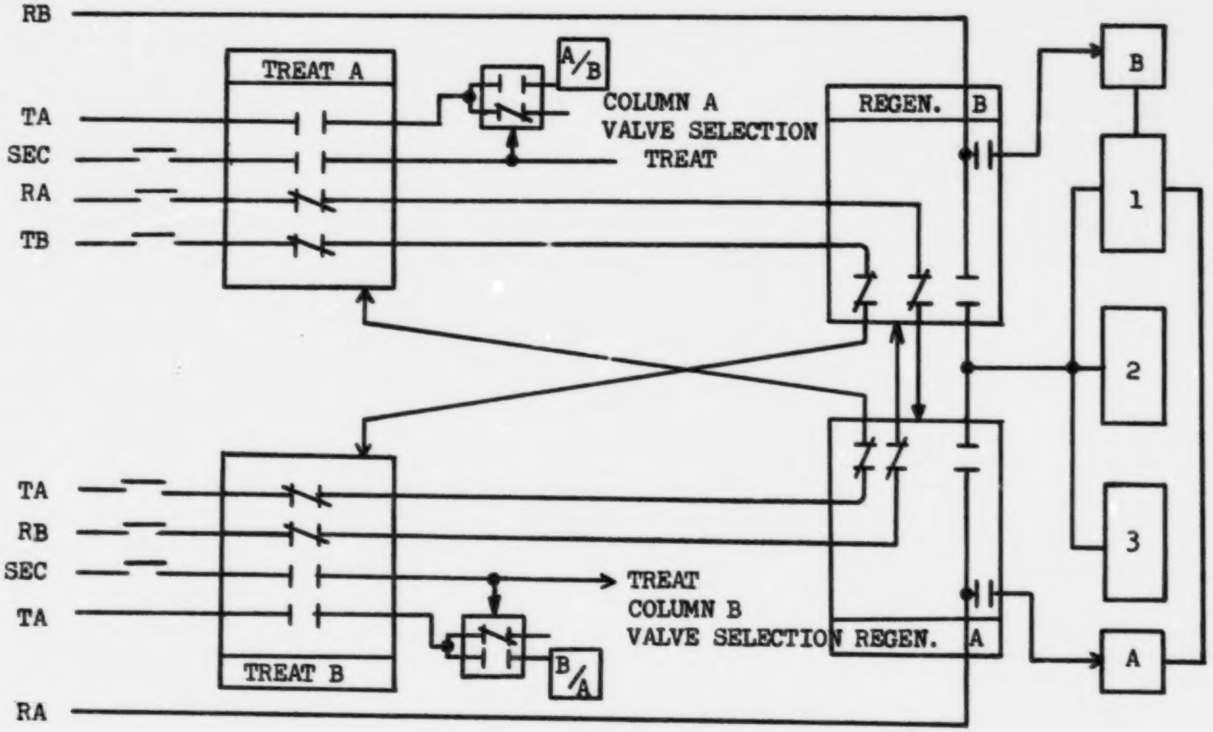

RB
TA
SEC
RA
TB
TREAT A
A/B
COLUMN A
VALVE SELECTION
TREAT
REGEN. B
B
1
2
3
A
TA
RB
SEC
TA
TREAT B
B/A
TREAT
COLUMN B
VALVE SELECTION
REGEN. A
RA

Figure 8   ILLUSTRATION OF THE SYSTEM OF INTERLOCKS (SEE KEY ON PAGE 30).

The lines of Figure 8 represent "hot" wires to the control system. The boxes represent relays. In some instances a current signal must be sustained once a given push-button is released. The current is sustained through self-energizing relays which are not shown.

If one pushes, for example, the RA push-button, this energizes the relay REGENERATE A. This cannot be done if either the TREAT A or the REGENERATE B relay is already actuated, because the normally-closed contacts of these latter relays will be open.

Key

RA	Regenerate Column A
RB	Regenerate Column B
TA	Treat Through Column A
TB	Treat Through Column B
SEC	Secondary Treatment, two columns in series.
A/B	Column A Ahead of Column B in series.
B/A	Column B Ahead of Column A in series.

Push-Button
Normally Open Contact
Normally Closed Contact
Wire Cross-Over With No Contact
Wire Cross-Over And Contact
Actuates A Given Relay

A	Valves and Level Controls for Regeneration of Column A.
B	Valves and Level Controls for Regeneration of Column B.
1	Sequencing Relay #1, Controls The Direction Of Flow Through The Resin Column. This Relay Also Stops Regeneration When The Last Required Event Is Satisfied
2	Sequencing Relay #2, Activates Pump 7 (See Figure 7), Acid Pump #2, The Main Water Valve, The Heat Exchanger And All Of The Bottom Valves On The Regenerant Storage Tanks. (i.e., Controls from where the regenerant solution is flowing.)
3	Sequencing Relay #3, Activates Pump 6 and All Of The Top Valves On The Regenerant Storage Tanks. (i.e., This controls to where the regenerant solutions will be pumped.)

KEY TO FIGURE 8, THE SYSTEM OF INTERLOCKS

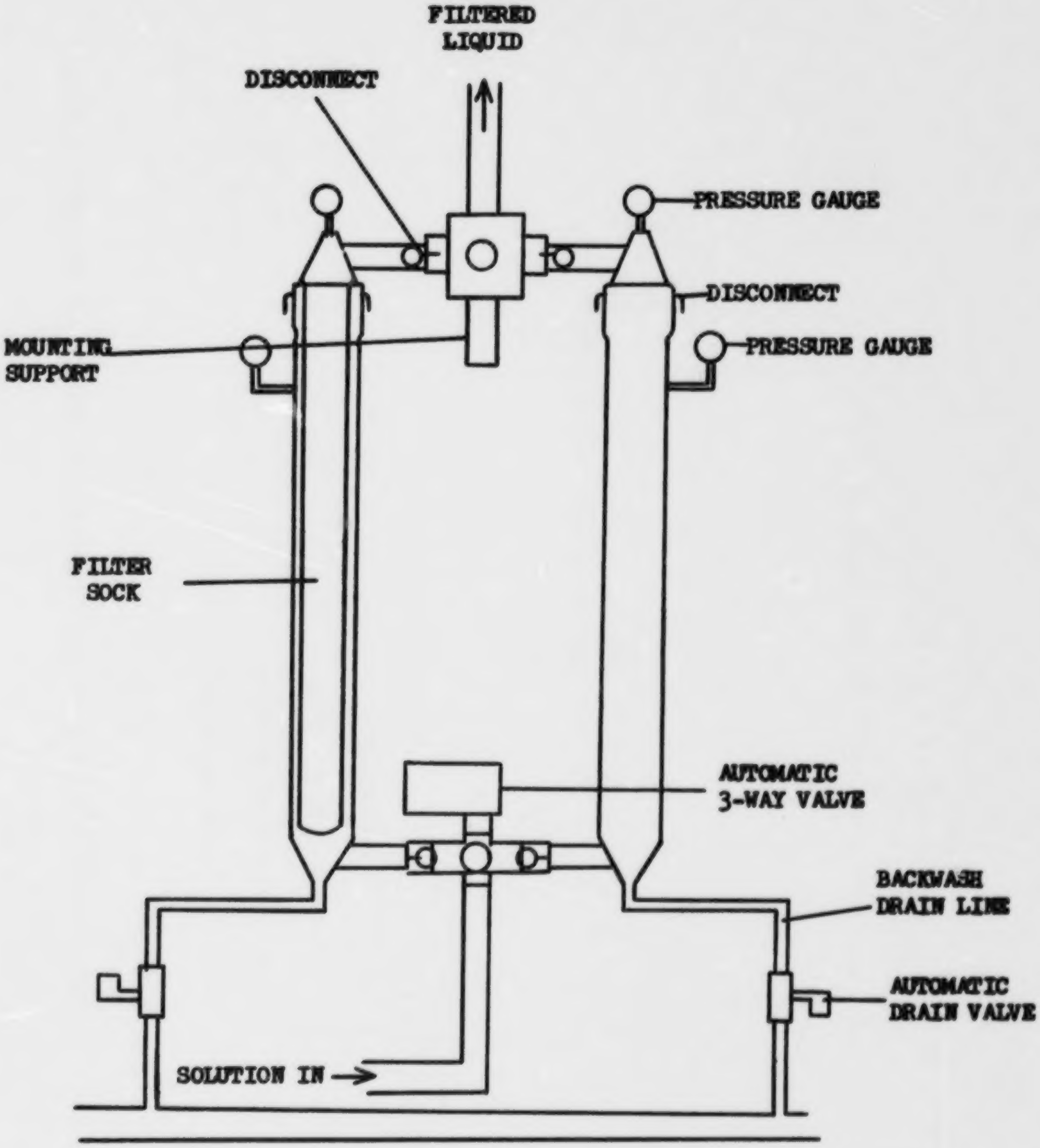

FILTERED LIQUID
DISCONNECT
PRESSURE GAUGE
DISCONNECT
MOUNTING SUPPORT
PRESSURE GAUGE
FILTER SOCK
AUTOMATIC 3-WAY VALVE
BACKWASH DRAIN LINE
AUTOMATIC DRAIN VALVE
SOLUTION IN

Figure 9 THE ARRANGEMENT OF THE SOCK FILTERS

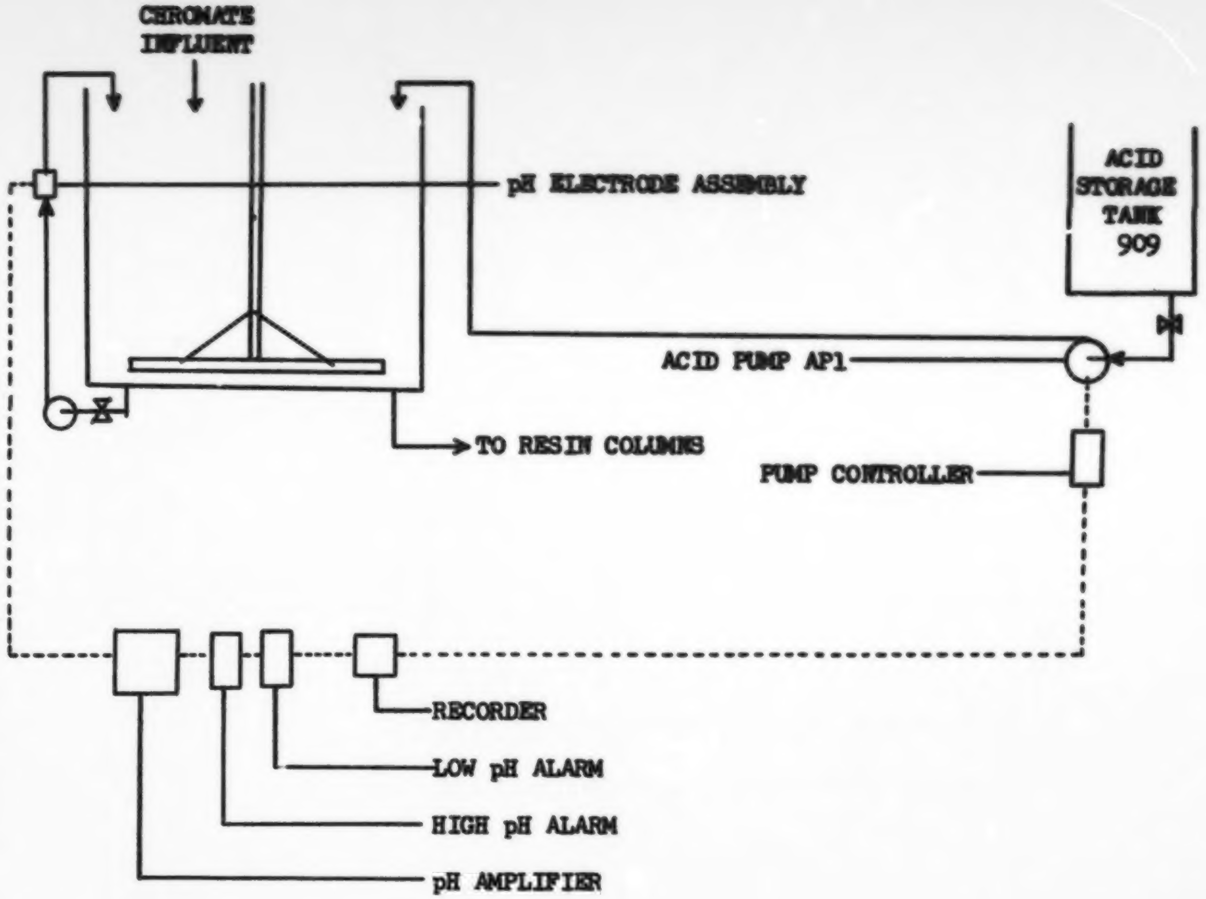

CHROMATE INFLUENT
pH ELECTRODE ASSEMBLY
ACID STORAGE TANK 909
ACID PUMP AP1
TO RESIN COLUMNS
PUMP CONTROLLER
RECORDER
LOW pH ALARM
HIGH pH ALARM
pH AMPLIFIER

FIGURE 10 ILLUSTRATION OF pH LOOP #1 WHICH CONTROLS THE INFLUENT TO THE RESIN COLUMNS

resin are less favorable. At a pH above 4.0 yellow pigment in suspension will accumulate between the resin beads in the column and cause an increase in the pressure drop across the resin bed. In the event the pH rises above 3.5, the high pH alarm will sound, again to demand operator attention.

A strip chart on the signal receiver records the influent pH continuously (See Figure 15.)

The second pH loop is shown in Figure 11. The discharge from the resin columns is directed through the colorimeter and delivered into Tank 911. The submerged pH electrode assembly is located at the bottom of this well-agitated vessel.

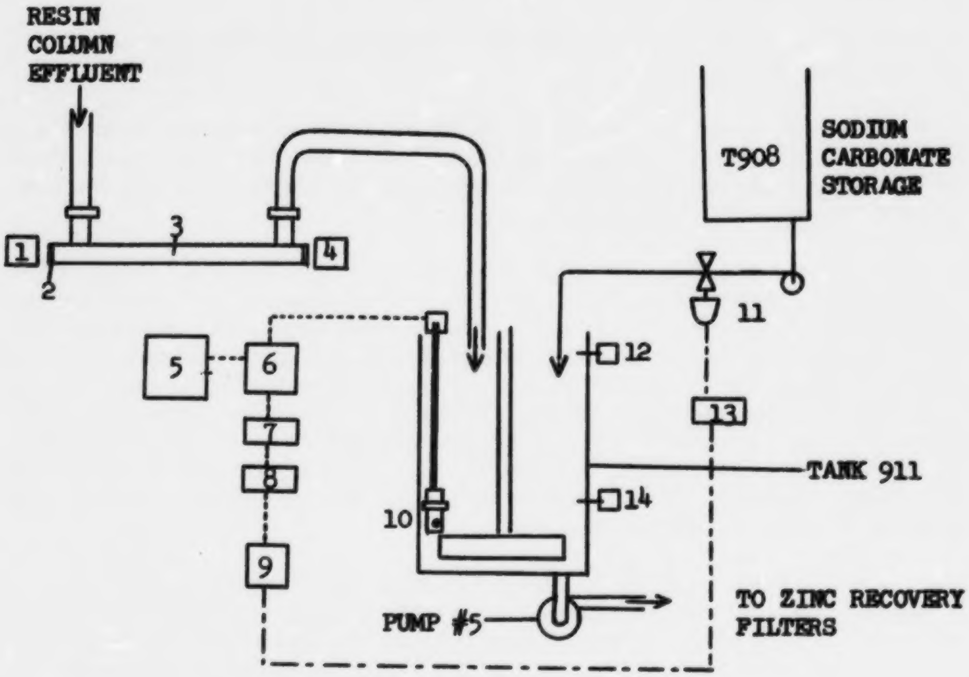
A 10 to 50 milliampere pH signal passes through a series loop which consists of the amplifier, the high and low pH alarms, a controller and the signal receiver (recorder). The current signal from the controller is converted to a 3 - 15 psig pneumatic signal by a current-to-pressure converter and the pressure signal is used to adjust a pneumatically actuated valve. Sodium carbonate solution is pumped from Tank 908 through this pneumatically controlled valve to the top of Tank 911. In Tank 911 the influent pH, normally 3.0, is adjusted until it is slightly alkaline. At a pH of 9.0 the zinc ion in the column discharge is precipitated as zinc carbonate.

The liquid level in Tank 911 is sensed by appropriately placed level probes. These probes actuate the on-off or pump-up, pump-down sequence of Pump 5. The pH of the waste solution, is thus continuously adjusted in Tank 911 and this tank is intermittently emptied as the solution is pumped to the zinc carbonate recovery filters.

The third pH measurement is made in a flow assembly in the discharge line from Pump 6 (shown in Figure 7). It is used to detect the point when the alkalinity of the regenerant solution has been neutralized and when the resin column has been re-acidified as required at the end of the regeneration process, before zinc-containing influent can be introduced to the resin column during the next treatment cycle. A low pH signal is used to start a timer which is used to determine the duration of dilute acid addition and recycling at the end of the regeneration process.

COLOR CONTROL

The dichromate ion is so highly colored that it can be determined colorimetrically[15]. Solutions to contain 1 ppm, 2 ppm, and 5 ppm of hexavalent chromium were prepared by dissolving carefully dried and weighed


RESIN
COLUMN
EFFLUENT
T908
SODIUM
CARBONATE
STORAGE
1
2
3
4
5
6
7
8
9
10
11
12
13
14
TANK 911
PUMP #5
TO ZINC RECOVERY
FILTERS

1 LIGHT SOURCE
2 FILTER
3 COLORIMETER LIGHT PATH
4 PHOTO CELL
5 RECORDER
6 pH AMPLIFIER
7 HIGH pH ALARM
8 LOW pH ALARM
9 CONTROLLER
10 pH ELECTRODE ASSEMBLY
11 PNEUMATICALLY ACTUATED NEEDLE VALVE
12 HIGH LEVEL PROBE
13 CURRENT-TO-PRESSURE CONVERTER
14 LOW LEVEL PROBE

FIGURE 11 ILLUSTRATION OF pH LOOP #2 WHICH CONTROLS THE COLUMN EFFLUENT

C.P. potassium dichromate in distilled water. These solutions were submitted to the colorimeter manufacturer and from these the appropriate color filter and the colorimeter light path were determined. A commercial turbidimeter was equipped with this blue filter and arranged with a forty-inch light path. This arrangement is capable of sensing as little as 1 to 2 ppm of chromium when the chromium is present as dichromate. Calibration of the colorimeter discharge by comparison with similarly prepared standard solutions has been repeated periodically.

Figure 11 illustrates the arrangement of the colorimeter. The entire flow from either of the resin columns (Tanks 905 and 906 in Figure 5) is directed through the colorimeter before the column effluent enters Tank 911.

There are two control points on the colorimeter. The first, usually set at 30-40% of full scale, is used to detect a bleeding of dichromate from a resin column. If this bleeding persists for longer than 30 seconds to one minute, the system automatically switches itself to secondary treat, thus directing the solution under treatment to a second resin column in series.

If the bleeding increases to sustained indicated levels above the second set point, this actuates a relay which sounds a "high color" alarm and turns off the treatment system. An operator is required to make an appropriate correction to the system and start the treatment cycle over again once this high color alarm has sounded.

Anything which interrupts the light path in the colorimeter is read by the instrument as color. Turbidity, air bubbles occluded in the resin column, oily films on the light path windows, abrupt temperature changes which cause condensation on the exterior of the windows and occasionally turbulent flow have each caused a "high color" alarm. Momentary "high color" signals (up to 60 seconds on a 0-60 second timer) alert the system operator without shutting the system down. If, however, the condition persists until the timer times itself out, the system shuts itself down automatically. These non-color interferences would make it impractical to utilize such a color control system with a 0.05 ppm chromium specification because the colorimeter signal at this sensitivity would "paint" the strip chart of the recorder.

Provisions are made to flush out the colorimeter with fresh water to permit start-up following a "high color" alarm. This is also available for cleaning both of the light path window, the window at the light source and the window at the photocell, both of which do require some periodic attention to prevent signal attenuation.

FLOW MEASUREMENT

Flow through the chromate recovery system is measured by conventional variable diameter flow meters. The entire influent flow passes a treatment flowmeter and the flow is controlled by a 3-inch manual gate valve. There is a similar arrangement for regenerant flow measurement and control. Wetted parts of the flowmeters are glass or 316 stainless steel. For this latter reason, the dilute acid solution required in the last step of resin regeneration bypasses the regenerant flowmeter.

LEVEL CONTROL

The automatic control of liquid levels in the chromate recovery system is necessary for satisfactory treatment and regeneration by automated control. This has presented a problem.

As first designed, all controlled levels were controlled by conductance probes installed in the walls of tanks. Where usable, conductance probes are the cheapest to buy and to maintain and the easiest to field wire. The solutions were "grounded" either by the wall of the tank, if the tank was metal, or by a probe introduced for this purpose in the non-metallic tanks. At 300 volts potential between the "probe" and the "ground", all liquids acted as current bridges sufficient to actuate relays on the control panel. However, settled solids, damp crystallized salts and liquid films also served as sufficient current bridges. In some cases, placing the probe in a PVC sheath and extending this sheath down to the desired level has worked. The arrangement is illustrated in Figure 12.

In the ion-exchange columns, particularly at the liquid-air interface an oily film or scum accumulates. This may be from lubricants used in the processing equipment, pump seals and the like and it may be due in part to the gradual break-down of the ion-exchange resin in contact with the acidic dichromate. This film fouls the conductance level probes and gives a false contact signal. In practice conductance probes and probes in sheaths have not worked well inside of the resin columns. Capacitance probes worked well and gave the "pump-up/pump-down" control capability when tried in one of the resin columns, but these probes, too, must be cleaned every two to three cycles. The capacitance level probes are thin and, of necessity, about six feet long and they can often suffer from physical damage as they are removed and replaced for cleaning.

We are currently evaluating sonic probes, which are to be installed at the desired liquid levels. Since they depend on the filling of a $\frac{1}{2}$" gap with vibration-transmitting liquid or solid, a fouling film should present no problem.

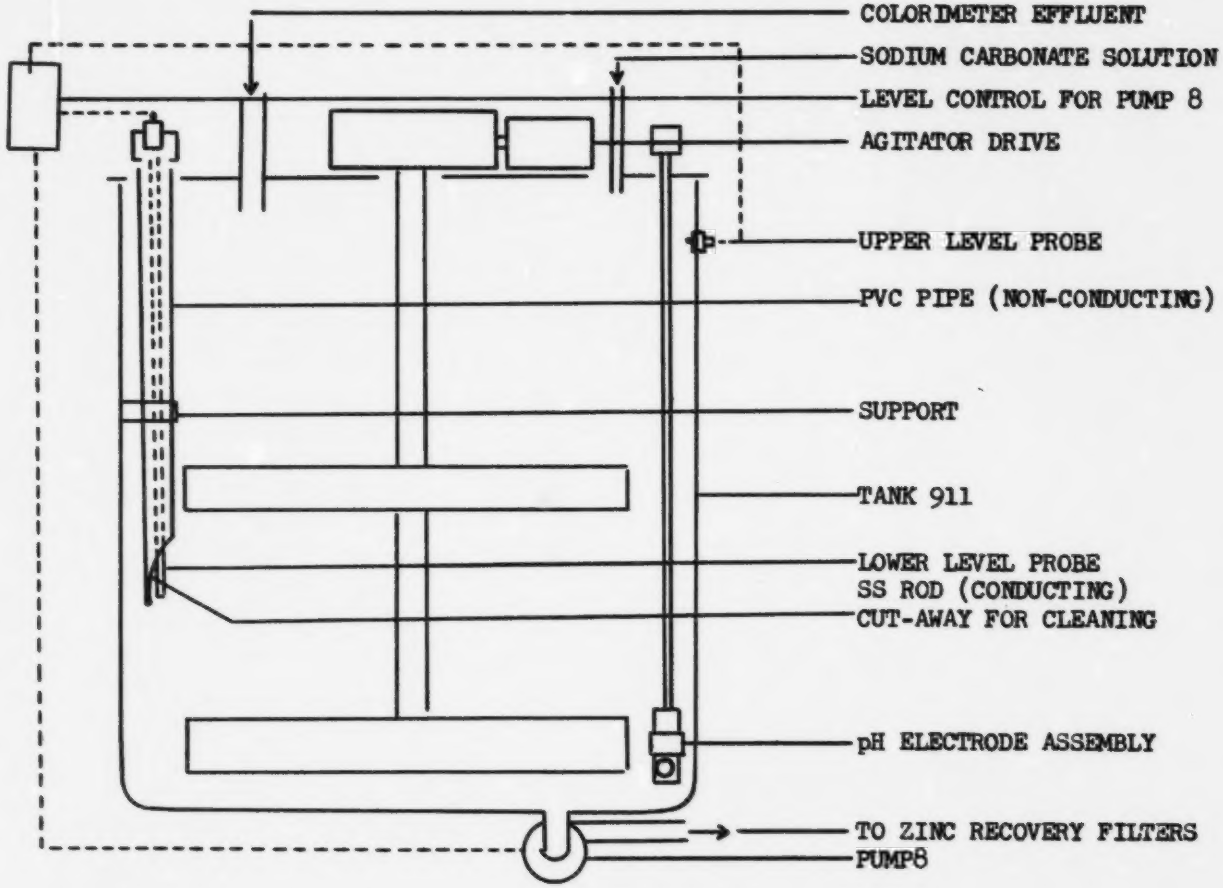

COLORIMETER EFFLUENT
SODIUM CARBONATE SOLUTION
LEVEL CONTROL FOR PUMP 8
AGITATOR DRIVE
UPPER LEVEL PROBE
PVC PIPE (NON-CONDUCTING)
SUPPORT
TANK 911
LOWER LEVEL PROBE
SS ROD (CONDUCTING)
CUT-AWAY FOR CLEANING
pH ELECTRODE ASSEMBLY
TO ZINC RECOVERY FILTERS
PUMP8

Figure 12 ILLUSTRATION OF THE LEVEL PROBES IN THE ZINC PRECIPITATION TANK

TEMPERATURE CONTROL

To maintain the regenerant temperature and the rinse water temperature at 50° C., we elected to use a shell and tube heat exchanger. The shell in the exchanger is of steel and the tubes are of copper.

During the regeneration steps which require heat, a main steam valve is automatically opened, and the opening of this valve activates the temperature control system. See Figure (13). The temperature control loop consists of a thermal bulb, which is the temperature sensing element, with a direct fluid connection to the bonnet of the steam control valve. The control valve regulates the input steam flow to the exchanger.

This loop would provide adequate control at a steady state condition, but since the time constant of the system is much shorter than the time constant of the controller, a forty-gallon surge tank was placed in the line. This insures that the resin and the PVC pipe downstream from the heat exchanger are completely protected from thermal damage.

A bi-metallic temperature switch, mounted at the surge tank outlet, is set to close the main steam valve if the outlet temperature rises above 60° C., the maximum recommended operating temperature for the ion-exchange resins.

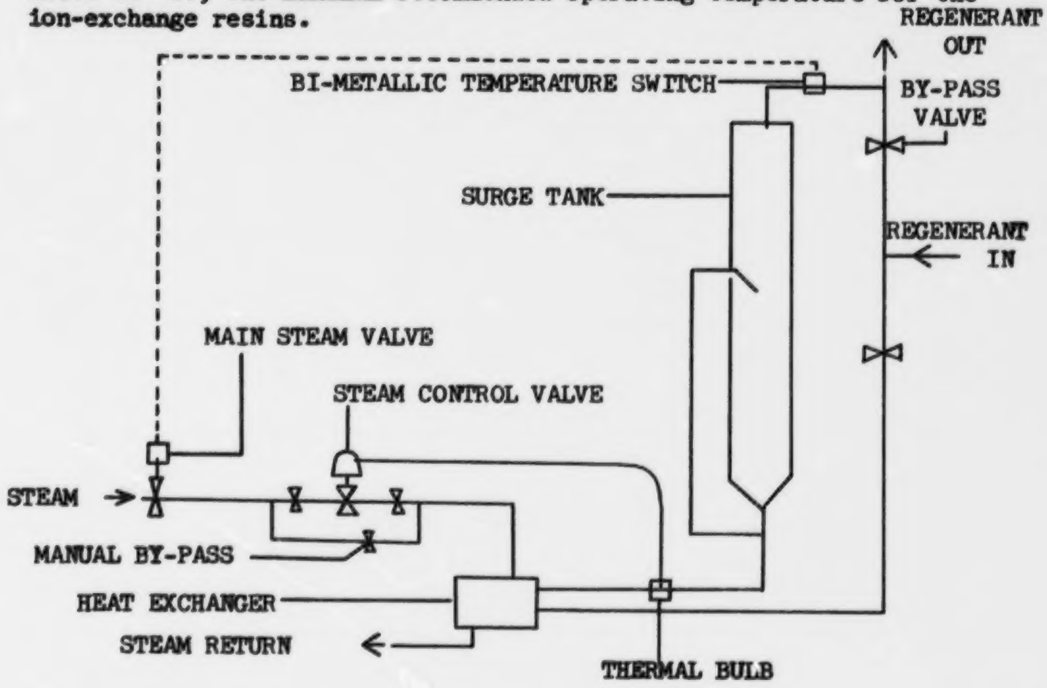

REGENERANT OUT
BI-METALLIC TEMPERATURE SWITCH
BY-PASS VALVE
SURGE TANK
REGENERANT IN
MAIN STEAM VALVE
STEAM CONTROL VALVE
STEAM
MANUAL BY-PASS
HEAT EXCHANGER
STEAM RETURN
THERMAL BULB

FIGURE 13   ILLUSTRATION OF THE TEMPERATURE CONTROL SYSTEM

PRESSURE AND VACUUM CONTROL

Shortly after the start-up of the system it became obvious that it would be necessary to install a pressure control system on the resin columns. The original resin columns were fabricated of fiber reinforced plastic and had a design range of -0.5 to +15 psi gauge pressure. We were experiencing pressure and vacuum readings outside of these limits. The pressures resulted from an accumulation of fine particles in the resin and the vacuum resulted whenever a bottom valve on a resin tank was opened while the tank was filled with liquid and the top valves were closed. This vacuum would have been sufficient to implode a partially filled tank or to collapse the dome-shaped cover.

The pressure control device consists of a ½ inch three-position electrically actuated valve mounted on the top of each of the resin columns. Position one on each valve is a closed position which isolates the column. The second position is a vent to the atmosphere. The vent pipe, however, is directed into the influent holding tank (Tank 2 of Figure 7) to contain liquids from a possible blow-back when the pressure is relieved. The third valve position makes a connection to a 12 psig air source. This enables one to pressurize the system to facilitate drainage of the column and to provide for an even down-flow of regenerant through the column.

The three-position valves are controlled by an electromechanical logic system which receives electrical signals from the process control relays and also from the high pressure and low pressure switches which are located above the respective resin columns as shown in Figure 14.

The high and low pressure switches, which are the primary sensing devices, are set at 15 psig and -0.5 psig (one inch of mercury), respectively. During treatment or regeneration a high pressure signal will; 1) cause an audible alarm, 2) display a visual indication of this high pressure problem on the alarm board, 3) turn the automatic pressure control valve to the vent position, and 4) cause an immediate shut-down of the treatment or regeneration through the column. During Secondary Treat there is a 30 second delay before shut-down. The high pressure in this situation may be due, not from a blockage, but from the additional pressure-drop of the second resin column in series. Similarly a low pressure signal will result in simultaneous alarm, light display, venting and immediate shut-down under any operating conditions.

Under normal operating conditions the top valve is in the closed position during treatment and secondary treatment. It is in the pressurized position during the steps of regeneration which involve flow out of the bottom of the column. The column is vented only during the water or regenerant filling steps of regeneration as we displace air from the resin bed.

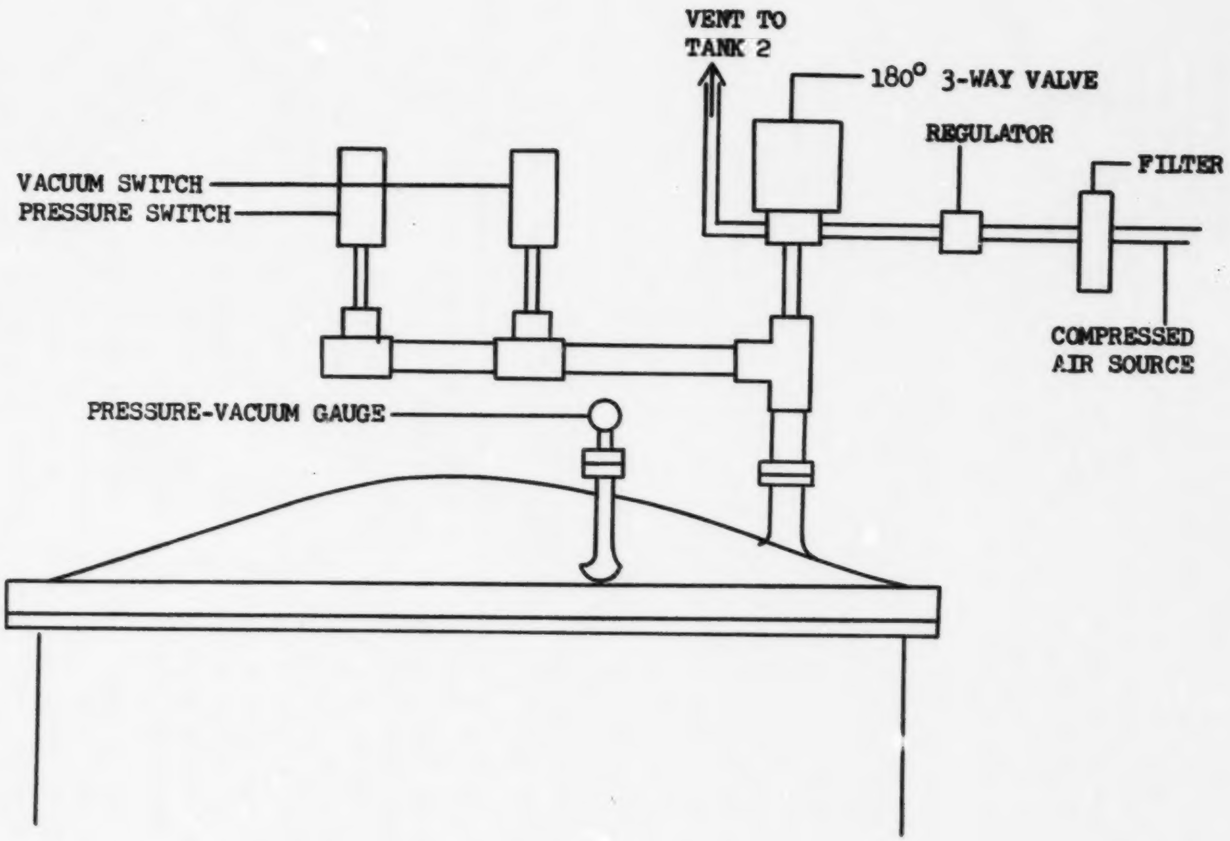

VENT TO
TANK 2
180° 3-WAY VALVE
REGULATOR
FILTER
VACUUM SWITCH
PRESSURE SWITCH
COMPRESSED
AIR SOURCE
PRESSURE-VACUUM GAUGE

FIGURE 14 ILLUSTRATION OF THE PRESSURE AND VACUUM CONTROLS ON THE RESIN COLUMNS.

Since the installation of the pressure control system we have replaced the fiber reinforced plastic resin (FRP) columns with epoxy coated carbon steel tanks which have much greater strength under pressure or vacuum. The tank covers are still the original FRP covers with nearly the same design limitations. In any case, we have found the pressure limits which were originally instituted to be acceptable process operating limits.

PLANT OPERATION

There was a considerable period of trial and error associated with the plant operation during its initial stages. Problems were experienced with:

1. Fine particles in the ion-exchange resin which plugged screen openings and created unexpectedly high pressures or low flows through the system.
2. Level probes. These problems were primarily with the probe becoming coated and giving a false contact signal.
3. The colorimeter, which does not differentiate between color and any other light interference, such as turbidity or air bubbles.
4. Failure to completely regenerate. This failure was caused by a variety of problems such as uneven flow distribution, improper drainage, too low a regenerant temperature, or a valve malfunction.

Each of these problems was solved, one by one, and the final plant design is such that a normal operation can be obtained by trained plant personnel with only a minimum of supervision.

During a typical month, one million gallons of influent are treated at an average flow rate of 55 to 60 gallons per minute. The chromium content of the influent varies from 1,200 parts of $Na_2Cr_2O_7 \cdot 2H_2O$ per million to 4,000 ppm. The average is about 1,800 ppm.

In a typical month we would recover 15,000 pounds of sodium dichromate for re-use in our pigment manufacturing operation. We would recover 18,000 pounds from a possible 19,000 pound (or 95%) of the potassium chloride which was used for the regeneration of the ion-exchange resin. In addition, we recover the zinc carbonate which precipitates from the chromium recovery treatment effluent on neutralization.

Figure 15 is a copy of the strip-chart recording. The left-hand line, which is green on our chart, is a measure of the influent pH on a scale of 1-5 pH units. It can be seen that the control loop #1 adequately controls the pH of the influent in this instance between 2.2 and 2.5.

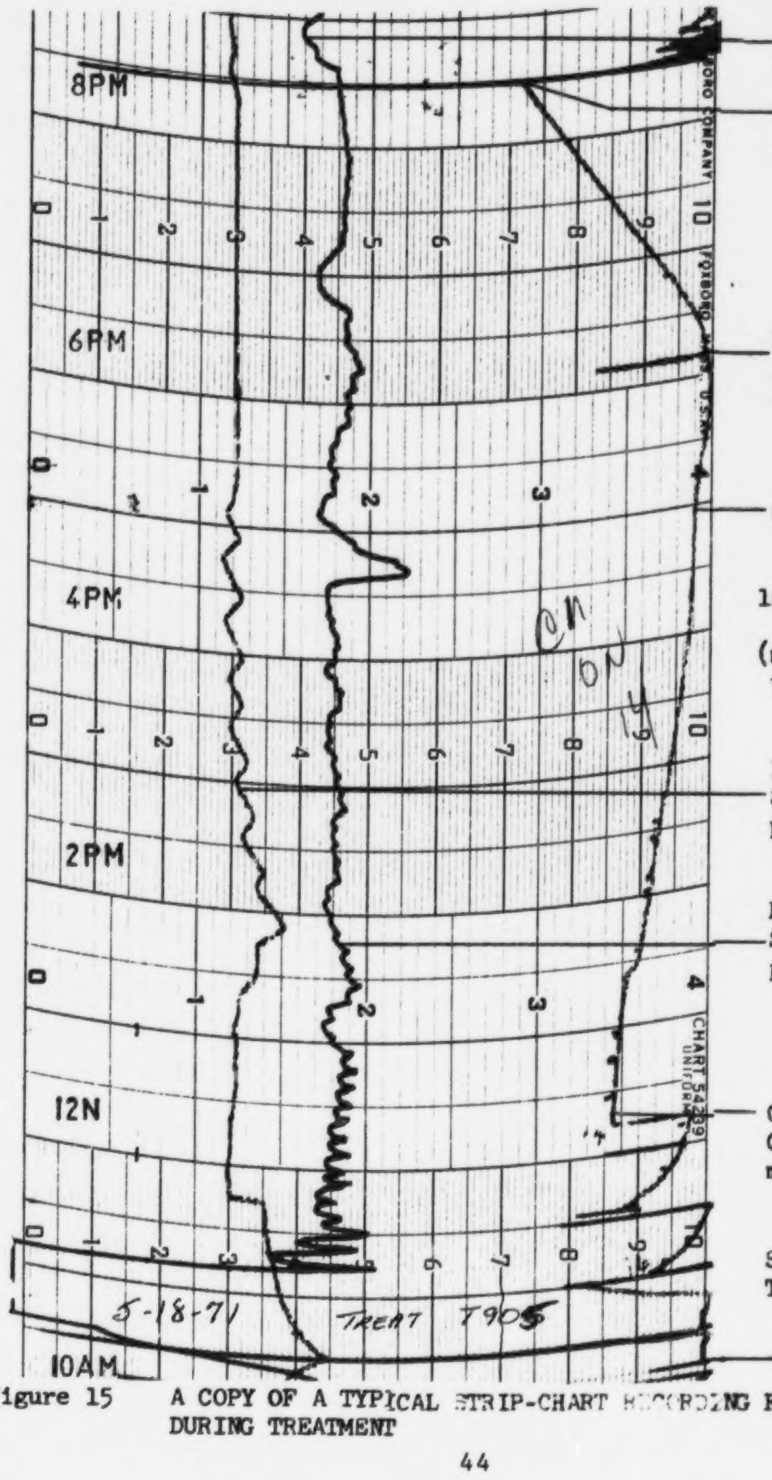
The center line (red on our chart) is a measure of the effluent pH on a scale of 5-9 pH units. This pH loop was set to control this pH between 6.6 and 7.3, and is normally quite close to 6.8.*

The right-hand tracing (blue on our chart) is a measure of freedom from the yellow (dichromate) color. At the start (10:30 A.M.) flow and air bubbles cause the reading to go to zero (maximum color) and quickly return. The steps in this tracing are caused by changing the "coarse" setting on the colorimeter. With the coarse setting on 14 the color was satisfactory from noon until 7:45 P.M.

At 7:45 P.M. a timer (initiated automatically from the colorimeter signal) timed out and transferred the system to "secondary treat" or treatment through the two resin tanks in series.

It can be seen that the color promptly returned to the satisfactory range (7 to 10). Acid from the acid rinse in Tank 906 was detected by the effluent pH loop, corrected, and the pH system also returned to normal.

*As noted elsewhere in this publication, the actual adjusted pH is normally 9.0. At some later point in time, it was discovered that the range of 6.6 to 7.3 did not consistently produce quantitative precipitation.



Acidity from Tank 906

Secondary Treat instituted

Flow interrupted as filter is cleaned

Color tracing
0 = maximum color
100 = minimum color
(maximum light transmitted)

Influent pH
Scale 1 to 5
pH units

Effluent pH
Scale 5 to 9
pH units

Colorimeter
Coarse adjustment on 14

Start of Treat
Tank 905

Figure 15 A COPY OF A TYPICAL STRIP-CHART RECORDING FOR THE SYSTEM DURING TREATMENT

DISCUSSION

SUCCESS OF THE PROJECT

Prior to the installation of this ion-exchange water treatment system, our procedure for disposing of the chromium in filtrates and wash liquors from the zinc yellow manufacture was as illustrated in equation (3) of the Introduction. The solution containing the chromate was acidified with sulfuric acid, then the resulting dichromate was reduced with sodium sulfite or sodium bisulfite. Following this reduction, the pH was raised to 8.5 to 9.0 with lime, and at this pH value essentially all of the chromium and the zinc were precipitated. This slurry of metal oxides or hydroxides and calcium sulfate was then concentrated and disposed of in a land-fill area. The installation of the ion-exchange treatment system has been beneficial to our overall plant operation from a number of points of view.

First, we are recovering raw materials (chromium and zinc) in useable form. The chromium, recovered as hexavalent sodium dichromate in nearly an 8% water solution, is immediately reuseable in the manufacturing process from which it originates. Its re-use has required no concession to product quality. The zinc, recovered as a mixed zinc hydroxide-zinc carbonate, is presently being evaluated by users interested in its zinc content.

Secondly, we have decreased significantly the quantity and particularly the volume of waste material which it is necessary to deposit in our land-fill area. Both chromium hydroxide and zinc hydroxide are precipitated as low solids, high volume products poorly suited for land-fill. Typically this mixed hydroxide precipitate will contain only 0.85% chromium. Were we to discard all of the chromium which we are currently recovering annually we would, on this basis, be discarding approximately 7,600,000 lbs of low solids sludge.

Thirdly, our plant operators have expressed an interest in the operation of the treatment system and they exhibit a greater willingness to get involved and assist us to maintain a quality effluent within the required guidelines. We have received many helpful suggestions from the plant operators which have in turn made the project more simple and more successful.

Finally, it is possible for us to attain discharge levels lower in both chromium and zinc than were attainable prior to the installation. This is true because the solid resulting from the conventional reduction-precipitation procedure from chromium waste treatment was allowed to settle in a lagoon.

At the time of treatment the removal of heavy metals was optimally complete, a function of pH and the presence or absence of competing or interfering ions. In the lagoon area, however, the settled solid was later subjected to contact with discharges from other operations in the plant. While these discharges were within, for instance, the pH guidelines of 5.5 to 8.5, a water solution at pH 5.5 will redissolve a significant quantity of zinc hydroxide from the lagoon and will actually be higher in zinc content than when originally discharged from the plant process. By removing these large quantities of both zinc hydroxide and chromium hydroxide from the lagoon this re-solution process has been shown to be diminished and both the zinc and chromium contents of the effluent are lower than they were prior to the installation.

PROSPECTS FOR THE AMORTIZATION OF THIS CAPITAL EXPENDITURE

Sodium dichromate is a $.16 per pound raw material. We estimate that it costs approximately $.25 per pound (chemical cost) to dispose of it in the above reduction-precipitation fashion. From Table 23 in Appendix C it can be seen that we recovered approximately 338,000 lbs of sodium dichromate in 23 months of operation, which is equivalent to 176,000 lbs per year. At $.25 per pound, this represents a saving of $44,000 per year. In addition to this, we are precipitating and recovering a saleable zinc carbonate which is estimated to sell between $25,000 and $45,000 on today's market. One additional saving is the cost of the by-product solids handling and disposal, which we estimate to be $14,000 per year. The total potential annual saving is, thus, in excess of $82,000.

The labor associated with running this plant is less than one man per shift, but the actual allocation would depend upon the plant's proximity to other units. If we assume no other duties are assignable to this individual, then the cost for the three-shift operation is estimated at $38,000 per year, for a net saving of over $44,000 per year. Thus to amortize the $125,000 expenditure will require less than three years.

APPLICATION TO OTHER INDUSTRIES

This study has been limited to the investigation of the use of ion-exchange resin in treating chromate-containing waste from a zinc yellow pigment plant. The original Nalco study dealt primarily with effluents from cooling towers and water from boiler blow-down in which chromates were used as corrosion inhibitors.

The secret to the utility of this technology is most certainly to find a use for the recovered chromate-containing regenerant solution. In this pigment plant application the conditions are not very favorable for exchange. That is, in the pigment plant application we experience chromate contents in the range of 1800 ppm and chloride ion concentrations as high as 21,000 ppm. (The chloride ion is approximately 0.36M.) If we were to assume that we would be faced with no less favorable conditions for exchange in some other industry than in our present application, it is reasonable that this exchange system would work to remove dichromate ions from other solutions requiring treatment.

Again, under the conditions reported here, we are accomplishing approximately a forty-fold concentration of the dichromate. If no use could be found for the recovered solution which contains approximately 8% potassium dichromate and 8% potassium chloride, then this solution, one-fortieth of its original volume, but still containing all of the original dichromate, would still have to be disposed of. This is generally done by reducing the dichromate to chromium (III), precipitating it as a hydroxide, filtering it or concentrating it in some fashion and finally disposing of it in a land-fill area. The same technique could probably be employed on the original solution prior to the ion-exchange treatment at a lower cost.

If a use can be found for the recovered chromate-containing solution, then this technique can be used wherever there is a chromate, dichromate, or chromic acid disposal problem. This would include the manufacturing processes for most chromate pigments, zinc chromate, basic zinc chromate, calcium chromate, barium chromate, strontium chromate, and chromium oxide.

Outside of the pigment industry this system might have utility wherever chromium is used as a corrosion inhibitor such as cooling towers and boiler feed waters, and where it is used as a raw material in the manufacture of a chromium-containing product, such as electroplating and unless there were interference from organic impurities, in tanning.

ATTAINING UNIFORM FLOW THROUGH THE RESIN BED

Doubtlessly our most troublesome problems were associated with our efforts to obtain uniform flow through the resin bed, a prerequisite for satisfactory regeneration. In the laboratory we dealt with 100 ml to 300 ml of resin. The resin was supported over glass wool and contained in a glass addition funnel. One could readily observe the flow, the color changes, channeling, back-wash, etc. As dichromate is adsorbed on the resin the adsorption is accompanied by a color change (as well as a change in the resin particle density). The pale straw yellow color of the freshly regenerated resin becomes a deep amber or orange-brown color when the resin is saturated with dichromate.

When, however, one places the resin in a five foot diameter resin column, an epoxy-lined steel tank, one can no longer make these helpful visual observations. Our first approaches were extremely naive in spite of much helpful advise[13,16]. We found liquids flowing through a resin bed to be extremely lazy, always content to take the path of least resistance, to channel along with what had preceded it. This was particularly true during upflow regeneration. In spite of considerable attention to the design and placement of the diffuser openings, we were repeatedly plagued with the inability to obtain a "water-white" effluent.

An accepted practice in many ion-exchange installations[17,18] is to place the resin on a porous sand support bed. The presence of the coarse sand is to assist the bottom diffuser in distributing the flow evenly across the entire cross-section of the bed. This assures that all of the resin is "active" and does not serve simply as an inert filler in the column. Because the sand is considerably more dense than the ion-exchange resin there is a minimum of mixing of the two media and any mixing which may occur on down-flow is essentially eliminated when the bed is back-washed. Thus the sand-resin interface remains quite distinct.

Our original column design incorporated a sand support bed to a level above the bottom diffuser openings. The presence of this carefully screened sand (from which all material smaller than 40 mesh had been removed) acted to plug the screen openings and to yield an unexpectedly high pressure drop. This pressure drop was observed even before the ion-exchange resin was added to the column.

The sand was removed to a level just below the bottom diffuser openings and the ion-exchange resin was added to the column. We operated for nearly six months with the sand support bed in place as illustrated in Figure 16. During this time we were constantly troubled by the presence of zinc yellow pigment which accumulated below the bottom diffuser. The zinc yellow which was in solution in the column influent was re-precipitated when the alkaline regenerant solution was added. In an insoluble form the zinc yellow was more difficult to remove from within the sand support bed. Its presence just below the bottom diffuser was apparent when acidified influent was re-introduced to the column. The acid-soluble pigment would slowly redissolve, migrate upward in the water solution and enter the column effluent as a hexavalent chromium discharge.

Efforts to flush the sand support bed upward or downward through the column's center bottom drain were only marginally successful and were very time consuming.

After what was thought by the operators to be a careful and thorough regeneration we would, upon occasion, sample the resin by driving an empty pipe through the depth of the bed, cap off the upper end of the pipe and withdraw it full of resin. The resin could then be examined both visually and by a laboratory-scale performance test to determine completeness of regeneration and to locate levels of poor flow and poor regeneration.

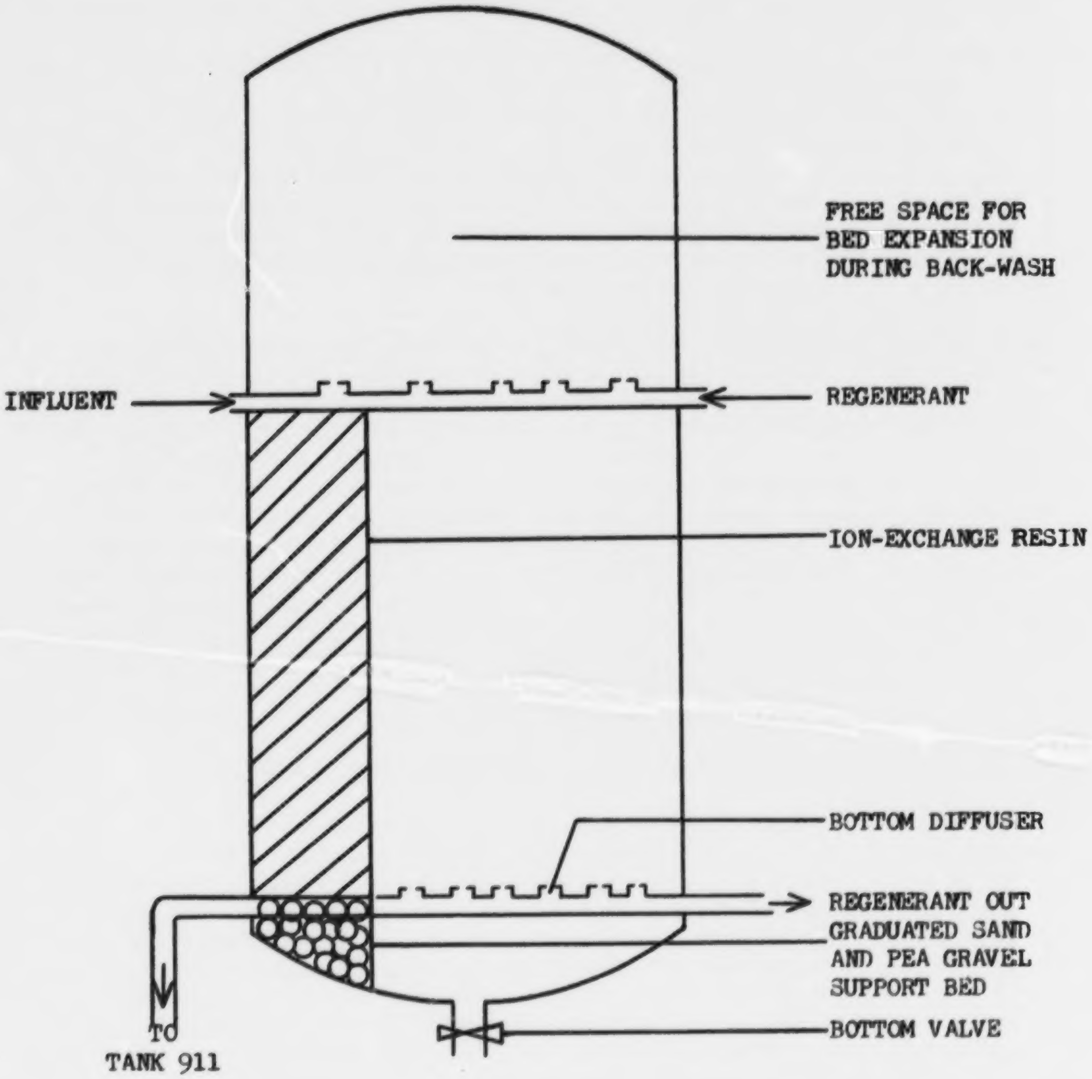

FREE SPACE FOR BED EXPANSION DURING BACK-WASH
INFLUENT
REGENERANT
ION-EXCHANGE RESIN
BOTTOM DIFFUSER
REGENERANT OUT
GRADUATED SAND AND PEA GRAVEL SUPPORT BED
BOTTOM VALVE
TO TANK 911

Figure 16 ILLUSTRATION OF THE RESIN COLUMN WITH SAND AND SUPPORT BED

Most of these problems were finally resolved when we removed the sand support bed and inverted the bottom diffuser, directing the openings toward the dish-shaped tank bottom. Down-flow from these openings now swept along the tank bottom, stirring the resin and contacting any potentially inert areas. The flow then changed direction and flowed upward toward the top diffuser. This change is illustrated in Figure 17.

The problem of displacing the dense regenerant salt solution upward from below by rinse water was only resolved by reversing the direction of flow. Normally one elects to regenerate in the opposite direction from the direction of treatment flow. This assures that the most satisfactorily regenerated resin beads will lie on the tank bottom in contact with the effluent and thus assures the minimum dichromate content in the effluent. Because of the previously mentioned density change, however, when the bed is back-washed the more dense (partially exhausted) resin beads find their way to the tank bottom.

Best regeneration results were obtained by down-flow regeneration also. If the chromium content of the regenerant solution toward the end of the regeneration process is not permitted to be too high (not above 1.5% sodium dichromate after use) one is generally assured of a complete regeneration throughout the entire column, and there is no significant dichromate concentration gradient throughout the resin bed. If there were a significant dichromate content remaining on the resin in the column, it would be necessary to retain this higher dichromate concentration at, or near, the top of the resin column; not at the bottom where it would be in contact with the column effluent. This is to say, only when one has eliminated partially regenerated resin within the column can one be assured that partially regenerated resin will not accumulate at the bottom of the column following back-wash.

THE SYSTEM OF SAFETY INTERLOCKS, ALARMS AND WARNING LIGHTS

Considerable attention was devoted, in the design stage, to make the system operable by relatively unskilled plant personnel. We were interested in safety and thus, for instance, we wanted to make it impossible to pump a concentrated alkali into a tank containing acids. We were interested in a quality effluent and we wanted to detect leaks and avoid spills. All of the effluent from the resin columns passes through the colorimeter so we are not troubled with by-pass sampling of the effluent stream. We paid particular attention to the concentrated chrome solution recovered from regeneration and made it impossible, for instance, for an operator to attempt to pump on top of an already filled tank.

We attempted to protect the equipment. In this system one cannot pump a dilute hydrochloric acid solution through a stainless steel valve, pump or flow meter. The system is protected against pressure levels and vacuum levels which are outside of the design specifications. PVC pipe and the ion-exchange resins are both protected from thermal damage.

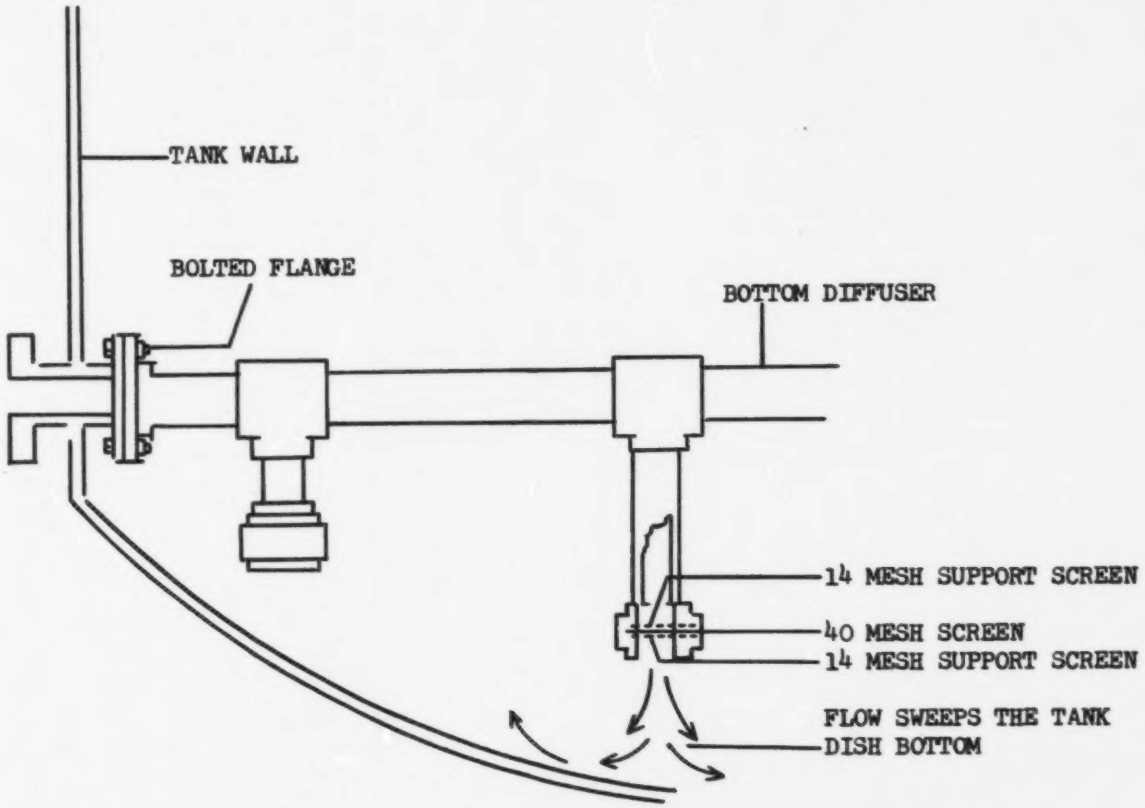

TANK WALL
BOLTED FLANGE
BOTTOM DIFFUSER
14 MESH SUPPORT SCREEN
40 MESH SCREEN
14 MESH SUPPORT SCREEN
FLOW SWEEPS THE TANK
DISH BOTTOM

Figure 17 ILLUSTRATION OF THE RESIN COLUMN AFTER REMOVAL OF THE SUPPORT BED AND INVERSION OF THE BOTTOM DIFFUSER

Finally, the operator is given assistance and some opportunity to anticipate problems. He cannot successfully call for regeneration if he has not re-made his regenerant solutions and emptied the storage tank which holds the recovered chrome solution. He is given warning when pH readings are outside of the control specifications and when his supply of sodium carbonate solution is being depleted. The following is a list of the safety interlocks, alarms and warning lights which were installed.

Interlocks

1. The recovered chrome solution tank (Tank 914 in Figure 7) is still full. The tank contents must have its pH adjusted to the dichromate pH and be pumped back to the manufacturing process before the next regeneration can be initiated.
2. The operator has failed to make appropriate additions of sodium hydroxide and potassium chloride to the regenerant holding tanks (Tanks 903 and 904 in Figure 7) after these tanks were re-filled with the column rinse water. The next regeneration cannot be started.
3. One cannot pump the zinc-containing influent on top of an alkaline regenerant solution. (One cannot treat through a particular column when that column is being regenerated, nor can one regenerate a column while it is still in use in treatment.)
4. One cannot regenerate a resin column when it is being used during secondary treatment. (During secondary treatment both of the columns are in use, so neither can be regenerated.)
5. One cannot regenerate two columns at the same time.
6. Except during secondary treatment, when the two columns are arranged in series, one cannot treat through two columns (in parallel) at the same time.
7. One cannot operate under pressure levels or vacuum levels outside of the design limits.

Alarms

The operator receives an audible alarm (which also sounds in the foremen's office) whenever:

1. The influent pH is too high.
2. The influent pH is too low.
3. The column effluent is too high in color.
4. The pH of the effluent from the zinc precipitation tank is too high.
5. The pH of the effluent from the zinc precipitation tank is too low.
6. Tank 914 (the recovered chrome solution tank) is still full.
7. Tanks 903 and 904 (the regenerant storage tanks for portions III and IV) have not been re-made.
8. Tank 908 (the sodium carbonate solution storage tank) is empty.

Warning Lights

Appropriately labeled warning lights are displayed on the control panel board to explain each of the above alarms, another to warn the operator of an imprudently low reserve of sodium carbonate solution and another to warn of a cautionary colorimeter response.

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13. Dickert, C. T., Rohm and Haas Company, Phila. PA, private communication with D. J. Robinson.

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GLOSSARY OF TERMS

Backwash - The process of flowing water upward through the ion-exchange resin bed to suspend the resin, remove resin fines and foreign matter, to render the column ready for its next treatment cycle.

Bleed - The situation wherein a visible low level of chromium (2 - 15 ppm) exists in the effluent from a resin column on treat.

Exhaust - The situation when the effluent from a resin column begins to approach the influent in visual appearance or in chromium content. The saturation of the column with respect to chromium uptake.

Regeneration - The process of removing adsorbed chromium from the ion-exchange resin and returning the resin to the chloride salt form. Regeneration is required once a column is exhausted.

Secondary Treat - The process of connecting two resin columns together in series so that the "bleed" from one column is collected in the second column when the two columns are on treat.

Treat - The process of flowing an acidified influent through a regenerated resin column in order to adsorb dichromate from the influent solution and thus remove this heavy metal contaminant from the effluent stream.

APPENDIX A

ANALYTICAL METHODS

ANALYTICAL METHOD FOR POTASSIUM

Reagents

1N acetic acid: 5.75 ml of glacial acetic acid is diluted to 100 ml with distilled water.

Sodium tetraphenyl boron reagent: Dissolve 0.15 g sodium tetraphenyl boron in 50 ml of distilled water.

Wash solution: Add a small amount of sodium tetraphenyl boron to 200 ml of distilled water containing a drop of HCl. Precipitate the reagent with KCl and filter. Shake the freshly precipitated potassium tetraphenyl boron with 500 ml of distilled water, filter to remove the excess solid and save the saturated wash solution.

Method:

Pipette 5.00 ml of the recovered potassium chromate solution, transfer to a 100 ml volumetric flask, and dilute to the mark. Pipette 5.00 ml of this diluted solution and transfer to a 250 ml beaker. Add 15 ml. of 1N acetic acid, 35 ml of distilled water, and, with stirring, 50 ml of the sodium tetraphenyl boron reagent. Filter immediately through a tared Gooch crucible. Dry in an oven above 100° C., but below 120° C. for one hour or to constant weight. Cool in a desiccator and weigh.

Calculation:

$$\frac{\text{Wt. of precipitate x } 0.2080}{0.25 \text{ ml}} \times 100 = \text{g KCl per 100 ml.}$$

ANALYTICAL METHOD FOR CHROMIUM

Reagents:

CP Potassium Iodide

6N Hydrochloric Acid; Dilute 500 ml of conc reagent grade HCl to one liter with distilled water.

Standard 0.1 N Sodium Thiosulfate Solution: Dissove 25 g of reagent grade sodium thiosulfate crystals $Na_2S_2O_3.5H_2O$ and 2 g of reagent grade sodium carbonate in one liter of freshly boiled distilled water. Store in a clean bottle, allow to cool and standardize with CP potassium dichromate.

Starch Indicator Solution: Paste 2 g of soluble starch in a small amount of water and add it to 100 ml of boiling distilled water. Add a small amount of mercuric iodide to prevent bacterial action.

Method:

Pipette 5.00 ml of the concentrated regenerant solution and transfer to a 100 ml volumetric flask. Dilute to the mark and mix thoroughly. Pipette from this flask a known aliquot to contain approximately 0.1 g of sodium dichromate. Dilute to 50 ml in a 250 ml iodine flask. Add 2 g of the potassium iodide and slowly, with swirling to avoid a localized excess, add 8 ml of the 6N hydrochloric acid solution. Titrate the iodine which is released at once with the standard sodium thiosulfate solution. Add the starch indicator about 1 ml prior to the end point. (The solution will have turned to a pale yellow-green color, but not the blue-green color of trivalent chromium.) The end point is determined by the disappearance of the deep blue color characteristic of starch in the presence of iodine.

Calculation:

$$\frac{\text{ml of } Na_2S_2O_3 \text{ x Normality x } 0.04967}{\text{ml of original sample in the aliquot}} \text{ x } 100 = \text{g } Na_2Cr_2O_7\ .2H_2O/100 \text{ ml}$$

APPENDIX B

DETAILS OF THE LABORATORY STUDY

REGENERATION OF THE ION-EXCHANGE RESIN

One of the first studies of the elutriation or regeneration of the ion-exchange resin was done by placing 300 ml of the resin in a tall, narrow column (one inch in diameter and 23½ inches deep). The column was exhausted by the introduction of an acidulated pigment waste solution which contained sodium dichromate. The column was then rinsed with distilled water and covered with a regenerant solution which contained 10 g KCl and 2.5 g NaOH per 100 ml. Every fifteen minutes a 10 ml portion of the regenerant solution was removed from the bottom of the column. The pH of each portion was measured and a 1.00 ml aliquot was titrated iodometrically to determine its dichromate content. A portion of the results of this study is recorded in Table 9 and the two curves, pH versus the volume of regenerant passed through the column and the concentration of the recovered regenerant solution versus the volume passed are plotted together in Figure 18 from this data.

Table 9 THE pH AND THE DICHROMATE CONCENTRATION OF SAMPLES OF THE REGENERANT SOLUTION PASSED THROUGH AN EXHAUSTED RESIN COLUMN TO STUDY THE REGENERATION PROCESS

Sample Number	pH	Titre* .1087 N $Na_2S_2O_3$	Concentration grams of $Na_2Cr_2O_7.2H_2O$ per 100 ml
5	3.0	0.00	0.000
10	6.0	0.00	0.000
15	7.3	0.61	.329
20	7.5	0.98	.529
25	7.5	1.12	.605
30	7.5	1.47	.794
35	7.6	1.80	.972
40	7.6	2.10	1.13
45	7.9	3.80	2.05
50	8.1	7.19	3.88
55	8.3	10.07	5.44
60	9.0	11.90	6.43
65	12.2	11.00	5.94

* 1.00 ml aliquot samples

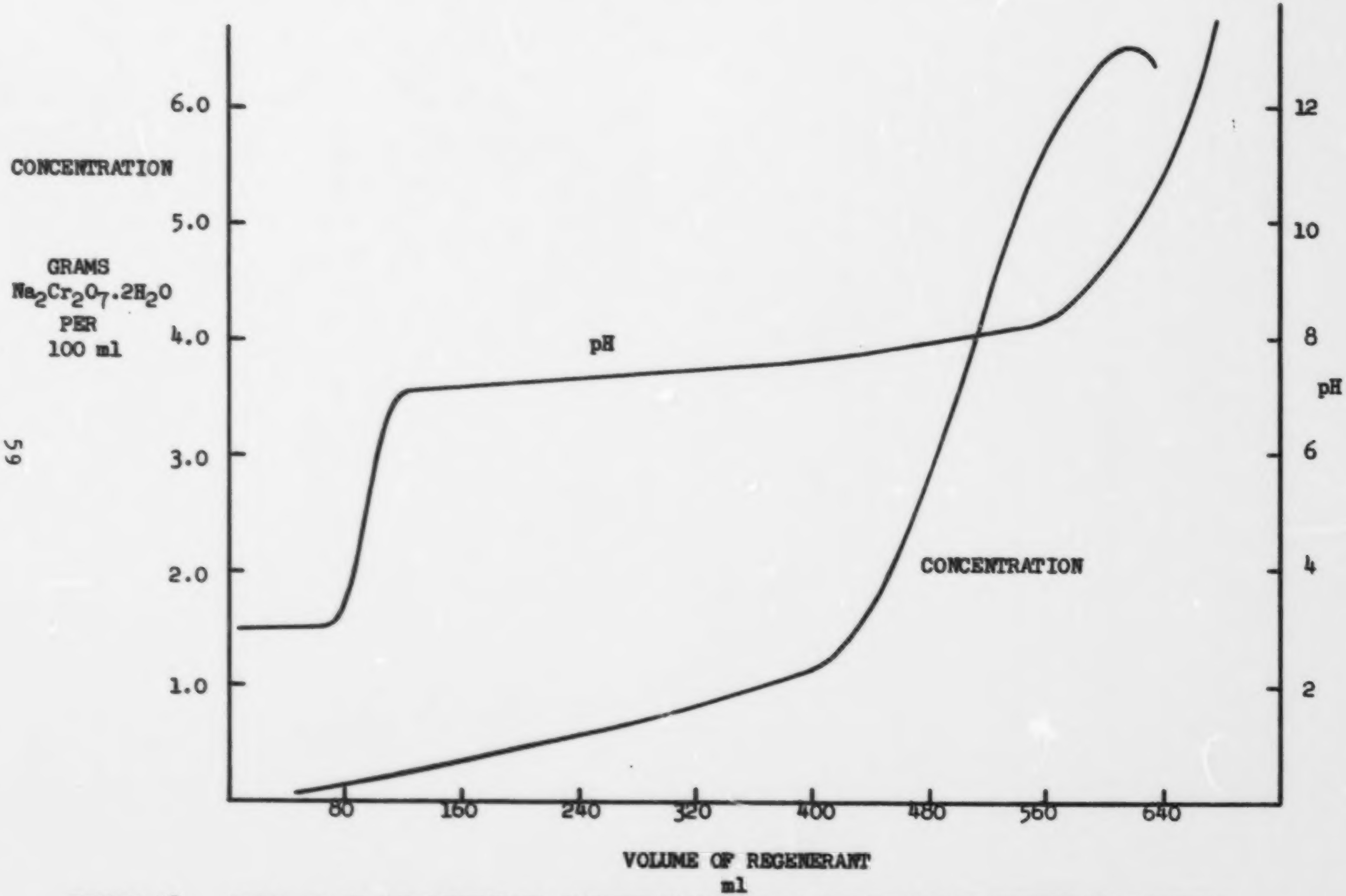

FIGURE 18 PLOTS OF pH AND DICHROMATE CONCENTRATION VERSUS THE VOLUME OF REGENERANT SOLUTION WHICH WAS PASSED.

It can be seen that the alkalinity of the regenerant is being consumed by the acidic dichromate which is adsorbed on the resin. When this dichromate acidity has been neutralized the rate at which the hexavalent chromium is being removed from the column increases, reaches a maxium and then drops off again. It should be noted that the abscissa is also a time axis since the samples were taken at fifteen minute intervals.

In the next study the column was again exhausted by the introduction of dichromate and then rinsed as before. This time, a 300 ml portion of regenerant, which contained 10 g KCl and 8 g NaOH per 100 ml, was introduced to hasten the neutralization of the column's acidity. This 300 ml portion was followed by regenerant which contained 10 g KCl and 2.5 g NaOH per 100 ml. Again a portion of the results are recorded in Table 10 and are plotted in Figure 19. It can be seen that the concentration maximum has been displaced toward the left, or that we have successfully removed a greater quantity of dichromate from the resin after only 320 ml has been removed, as compared with 600 ml during the previous test. It should be pointed out that the concentration scales of Figures 18 and 19 are not the same. The concentration of the recovered regenerant is in part a function of the quantity of dichromate present on the column prior to the regeneration.

Table 10 THE pH AND THE DICHROMATE CONCENTRATION OF SAMPLES OF REGENERANT WHEN EXCESS ALKALI IS ADDED INITIALLY

Sample Number	pH	Titre* .1015 N $Na_2S_2O_3$	Concentration grams of $Na_2Cr_2O_7.2H_2O$ per 100 ml
3	6.0	0.00	.000
5	7.9	4.20	2.12
10	9.3	22.80	11.5
15	9.4	25.19	12.7
20	9.3	30.13	15.2
25	9.3	32.09	16.2
30	9.3	32.25	16.3
36	12.1	25.35	12.8

* 1.00 ml aliquots

Table 11 and Figure 20 which were accumulated from data from the regeneration of a partially exhausted column are included only to show that the concentration curve when completed is essentially symmetrical about the concentration maximum and the maximum occurs in a much narrower region when the larger quantity of base is used in the regenerant. This column was regenerated entirely with a solution which contained 10 g KCl and 8 g NaOH per 100 ml.

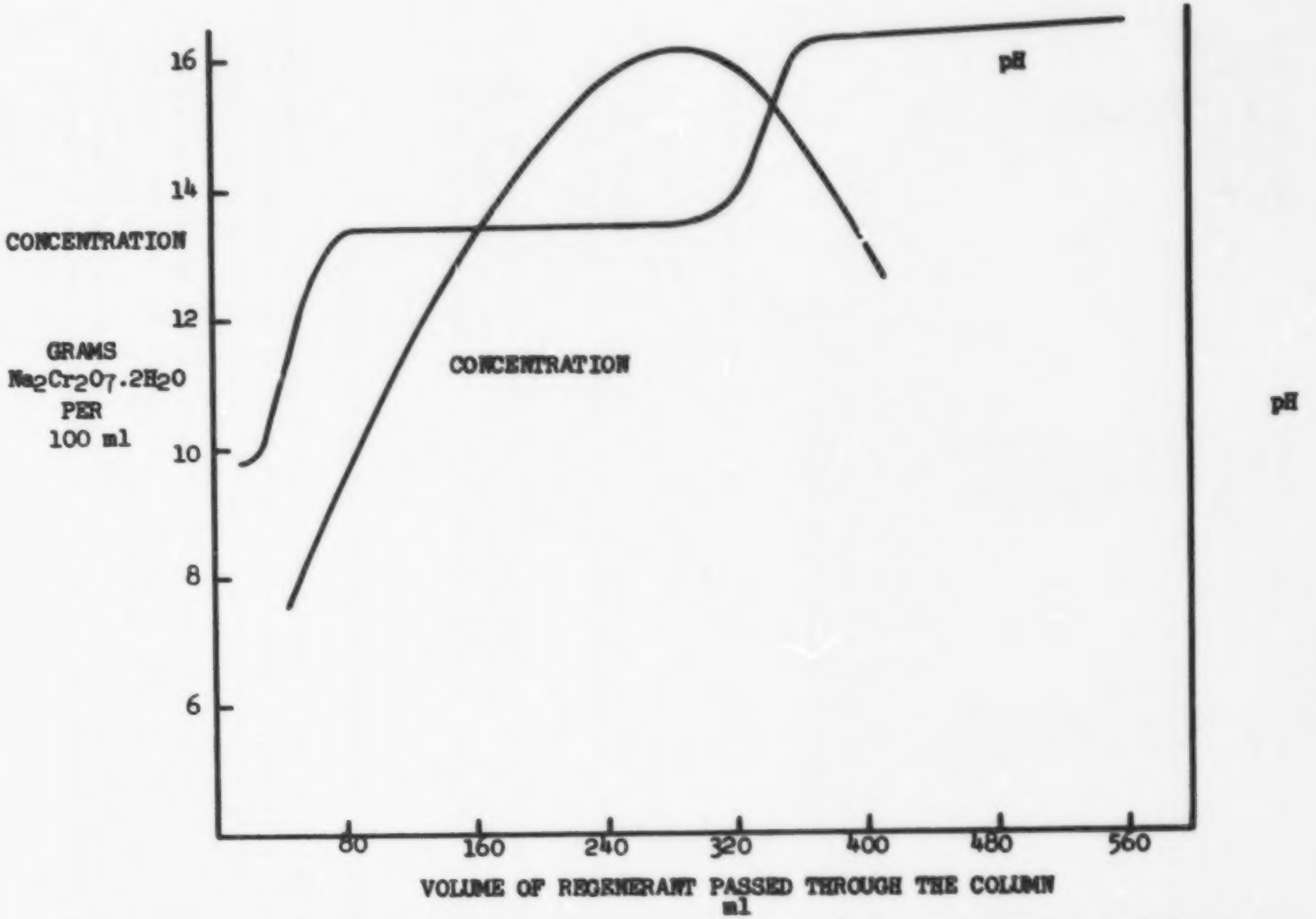

FIGURE 19 PLOTS OF pH AND DICHROMATE CONCENTRATION VERSUS THE VOLUME OF REGENERANT SOLUTION PASSED. EXCESS ALKALI WAS ADDED IN THE FIRST 300 ml

Table 11 THE pH AND THE DICHROMATE CONCENTRATION OF SAMPLES OF REGENERANT WHEN EXCESS ALKALI IS ADDED AND WHEN THE COLUMN, INITIALLY, IS ONLY PARTIALLY EXHAUSTED

Sample Number	pH	Titre* N** $Na_2S_2O_3$	Concentration grams of $Na_2Cr_2O_7.2H_2O$ per 100 ml
5	4.1	0.00	.000
10	6.0	0.81	.076
15	7.0	2.44	.228
20	7.1	4.11	.385
25	7.4	12.71	1.19
30	7.6	11.61	1.09
35	9.4	28.20	2.71
40	12.7	18.72	1.80
45	12.8	7.53	.723
48	12.8	4.5	.432

* 5.00 ml aliquots

** For samples 1-31 the Normality was 0.09423
For samples 32-48 the Normality was 0.09664

There is now an economic consideration. The raw material which is required in the manufacture of the zinc yellow pigment is sodium or potassium dichromate, not chromate, and any excess base present in the recovered regenerant solution must be acidified before the accompanying hexavalent chromium can be used. That is to say, it is necessary to neutralize the excess alkali in order to convert the chromate present to dichromate.

As mentioned earlier in this report, an economy was realized by recycling the first portion of regenerant through the column, a technique which assures the maximum chromium content and the minimum quantity of excess base in the recovered solution.

CONCENTRATION OF DICHROMATE IN THE RECOVERED REGENERANT

In Tables 12, 13 and 14 are recorded the concentrations of sodium dichromate in the recovered regenerant solutions. In each regeneration there are four equal-volume portions. Portions I and II, which have the highest chromium content and the minimum of excess free base, are returned to the manufacturing process for re-use. Portions III and IV from one regeneration become portions I and II respectively for the next regeneration. Table 12 shows the data from regeneration of the Rohm and Haas resin. Tables 13 and 14 are both developed from data from regeneration of the Dow resin and illustrate a range of variation from sample to sample. The

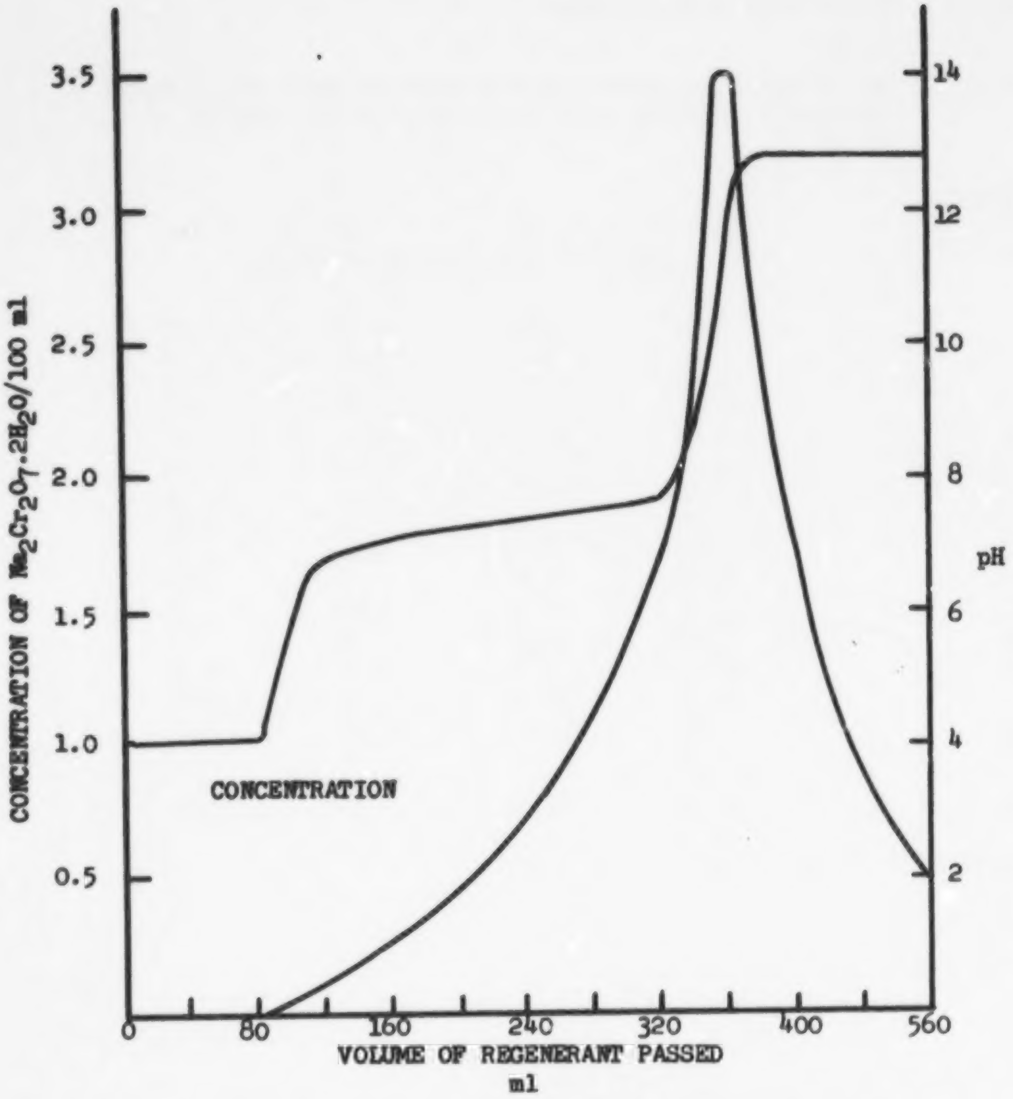

Figure 20 PLOTS OF pH AND DICHROMATE CONCENTRATION VERSUS THE VOLUME OF REGENERANT SOLUTION PASSED. EXCESS ALKALI WAS ADDED TO A PARTIALLY EXHAUSTED COLUMN.

actual plant experience with the Dow resin (shown in Table 14 of Appendix B) is closer to the new sample. Portions I and II are combined prior to re-use, so the average analysis of these portions is what should be compared with the reported plant results.

Table 12 THE SODIUM DICHROMATE CONCENTRATION OF EACH OF THE FOUR REGENERANT PORTIONS USED TO REGENERATE THE ROHM AND HAAS RESIN

Portion No. Cycle No.	I	II	III	IV
	grams of $Na_2Cr_2O_7.2H_2O$/100 ml			
1	6.49	4.33	2.16	1.27
2	6.61	3.80	1.98	1.08
3	6.73	4.22	2.22	1.06
4	6.44	4.04	2.06	0.98
5	6.75	4.12	2.31	0.83
6	6.28	4.25	2.06	0.90
7	6.68	4.19	2.32	1.16
8	6.95	4.14	2.38	0.69
9	6.63	4.13	1.93	1.08
10	6.92	3.84	1.96	1.07
11	6.63	4.37	2.29	1.16
12	7.28	3.92	1.76	1.17
13	6.68	4.14	1.96	1.01
14	6.78	4.04	1.92	0.85
15	6.99	3.90	2.26	1.05
16	6.58	4.87	2.82	1.31
Average	6.71	4.14	2.15	1.04
Portions I and II combined		5.43		

Table 13 **THE SODIUM DICHROMATE CONCENTRATION OF EACH OF THE FOUR REGENERANT PORTIONS USED TO REGENERATE THE DOW RESIN (ORIGINAL LABORATORY SAMPLE)**

Portion No.	I	II	III	IV
Cycle No.	grams of $Na_2Cr_2O_7.2H_2O$/100 ml			
1	9.26	4.98	2.44	1.10
2	9.56	5.43	2.40	1.36
3	9.56	5.82	2.74	1.19
4	9.90	6.22	2.60	1.24
5	9.61	5.84	2.34	1.15
6	8.88	5.85	2.81	1.05
7	9.06	4.43	2.14	1.15
8	8.73	5.18	2.58	1.09
9	9.03	5.62	2.84	1.15
10	8.96	5.63	2.39	1.19
11	8.85	5.02	2.50	1.15
12	8.71	5.33	2.25	1.00
13	9.07	5.11	2.40	1.15
14	8.51	5.15	2.30	1.16
15	9.70	5.78	2.35	1.25
16	8.75	5.55	2.75	1.34
17	9.21	5.70	2.73	1.52
Average	9.14	5.45	2.50	1.19
Portions I and II combined		7.30		

Table 14 THE SODIUM DICHROMATE CONCENTRATION OF EACH OF THE FOUR REGENERANT PORTIONS USED TO REGENERATE THE DOW RESIN (NEW PLANT SAMPLE)

Portion No.	I	II	III	IV
Cycle No.	grams of $Na_2Cr_2O_7 . 2H_2O$/100 ml			
1	11.25	6.83	3.39	1.86
2	11.55	7.55	4.03	2.31
3	10.96	7.13	3.28	2.14
4	10.60	7.39	4.23	2.14
5	10.38	7.02	3.58	1.94
6	10.65	7.06	2.99	2.23
7	10.74	6.84	3.19	1.75
8	10.53	7.27	3.83	1.57
9	10.80	6.72	3.78	1.97
10	11.24	6.46	3.65	1.79
11	10.60	6.51	3.35	1.86
12	10.26	5.85	2.88	1.70
13	10.55	6.16	3.23	1.90
14	10.65	6.41	3.10	1.56
15	10.38	6.40	3.75	1.88
16	9.51	6.19	4.06	2.45
17	10.66	6.65	3.65	2.30
Average	10.67	6.73	3.53	1.96
Portions I and II combined		8.70		

DETAILS OF THE ACCOUNTING FOR DICHROMATE INTRODUCED IN THE INFLUENT

As indicated earlier in the report, we adopted as a laboratory procedure for regeneration of the exhausted resin the use of four 100 ml portions of regenerant solution to regenerate a 100 ml resin column. The first two portions of regenerant which contained the highest concentrations of recovered dichromate were intended for recycle to manufacturing. Portions three and four from one regeneration would become portions one and two respectively for the next regeneration. Each portion of regenerant was analyzed for its chromium content and the results for one day (3/12/70) were recorded as in Table 15.

Table 15 CHROMIUM ANALYSES FOR THE FOUR REGENERANT PORTIONS USED TO REGENERATE THE DOW RESIN 3/12/70

Sample Number	Aliquot	Titre .1089 N $Na_2S_2O_3$	Weight of Sodium Dichromate in 100 ml
B4	1.00	11.91	6.44 g
B5	1.00	8.51	4.60
B6	1.00	5.30	2.87
B7	1.00	2.91	1.57

The calculation of Table 15 is done as follows:

$$\frac{\text{Titre x Normality x Milliequivalent Wt.}}{\text{Aliquot}} \text{ x Total Volume} = \text{g } Na_2Cr_2O_7.2H_2O \text{ in the sample}$$

Substituting the values for sample B6 of Table 15 we obtain:

$$\frac{5.30 \text{ x } .1089 \text{ x } .04967}{1.00} \text{ x } 100 = 2.87 \text{ g } Na_2Cr_2O_7.2H_2O$$

On the next day (3/13/70) the following were recorded:

1) The influent concentration:
A 10 ml aliquot of the influent required 20.41 ml of .1089 N sodium thiosulfate solution in the iodometric titration.

$$\frac{20.41 \text{ x } .1089 \text{ x } .04967}{10.00} = 0.01104 \text{ g } Na_2Cr_2O_7.2H_2O/\text{ml}$$

2) Total dichromate in the influent:
The 100 ml Dow resin column was exhausted by 1400 ml of the above influent solution, so the total dichromate in the influent was:

$$1400 \text{ ml x } 0.01104 \text{ g/ml} = 15.46 \text{ g } Na_2Cr_2O_7.2H_2O$$

3) Dichromate recovered:
Regenerant portions B6 and B7 from the previous regeneration cycle were reused and portions B8 and B9 which were freshly prepared were then used to regenerate the exhausted resin column. The dichromate analyses for these solutions, the rinse and back-wash are recorded in Table 16.

Table 16 CHROMIUM ANALYSES FOR THE REGENERANT SOLUTIONS USED TO REGENERATE THE DOW RESIN 3/13/70

Sample Number	Aliquot	Titre .1089 N $Na_2S_2O_3$	Total Volume	Weight of $Na_2Cr_2O_7.2H_2O$ Recovered
B6	1.00 ml	13.34 ml	100.0 ml	7.22 g
B7	1.00	10.50	100.0	5.68
B8	1.00	5.09	100.0	2.75
B9	1.00	3.25	100.0	1.76
Rinse	1.00	1.66	100.0	.898
Backwash	50.00	1.00	500.0	.054
Total Dichromate Contained				18.36 g

4) Net Dichromate recovered:
Regenerant portion B6 contained 2.87 g and B7 contained 1.57 g of dichromate from the previous regeneration which total 4.44 g. If we subtract this amount from the total dichromate from Table 16 we have a net value of 13.92 g. This amounts to 90% of the influent dichromate. (i.e., 13.92 is 90% of 15.46))

On a given day, primarily because the "exhaust" point was determined visually, we could account for as little as 90% of the dichromate, or as much as 108%. Over fifty-eight cycles, however, it can be seen from Table 17 that we accounted for 99.5% of the dichromate which was introduced in the influent as being recovered either in the regenerant or in the rinse and back-wash waters.

Table 17 AN ACCOUNTING FOR THE INFLUENT DICHROMATE IN THE RECOVERED REGENERANT

(grams of $Na_2Cr_2O_7.2H_2O$)

Rohm & Haas Resin		Dow Resin	
Dichromate in influent	Dichromate[a] recovered	Dichromate in influent	Dichromate[a] recovered
9.18	9.53	19.21	19.15
11.73	12.47	12.92	13.53
8.90	9.27	14.06	14.10
11.39	11.97	11.55	12.70
8.90	9.27	16.02	16.00
11.39	11.78	12.82	12.95
8.90	8.91	16.91	15.62
11.74	11.56	13.12	12.92
9.43	9.40	17.62	17.39
11.39	11.34	13.27	13.40
8.72	9.21	18.15	17.04
11.39	11.55	13.27	13.40
9.07	9.64	18.15	16.99
12.46	13.06	14.22	13.96
8.90	9.02	18.15	17.77
11.03	11.51	13.17	13.26
9.61	10.38	12.46	11.85
8.18	8.47	18.15	18.35
10.72	10.71	12.62	12.28
7.95	8.51	16.78	16.78
11.40	11.18	12.69	12.49
7.99	7.73	18.33	17.73
12.11	12.59	13.11	12.26
7.61	7.02	17.99	17.11
12.45	11.30	12.80	12.52
9.16	8.74	16.57	16.79
11.93	11.94	13.32	13.15
8.83	8.79	18.76	18.12

Total dichromate in influent	736.59 g
Total recovered dichromate	733.28
Percentage recovery	99.55%

a: Total (net) recovery in four regenerant portions plus the rinse and backwash solutions.

APPENDIX C

DETAILS OF THE PLANT OPERATIONS

INFLUENT ANALYSES

In Table 18 we have recorded one month's influent data. Again we can observe variations from 965 ppm to 3286 ppm, with the average figure 1952 ppm quite close to the figure of 1927 ppm reported in our laboratory work in Table 18. As in the laboratory study we had one instance where color was introduced in error into the waste recovery system. This time analyses of 8472 and 15,376 ppm were recorded. These concentrations for a brief period presented no problem to the recovery system.

RESIN EXCHANGE CAPACITY

One means of estimating the exchange capacity of the ion-exchange resins is to determine the quantity of sodium dichromate recovered from the exhausted column. This data is reported in Table 19.

THE CONCENTRATION OF THE RECOVERED REGENERANT SOLUTION

The regenerant solution which is originally composed of 8% KCl and 2.5% NaOH, contains potassium dichromate, excess potassium chloride and sodium hydroxide after it has been used to regenerate an ion-exchange resin column. In our efforts to re-use this solution we are concerned with a number of considerations: 1) The potassium content. Potassium, as either potassium chloride or potassium chloride, is a required raw material in the zinc yellow manufacture. 2) The dichromate content. Sodium dichromate or potassium dichromate can be used in the zinc yellow manufacture. 3) Excess base. The required raw material is sodium dichromate, not sodium chromate, and any excess base must be acidulated to the dichromate pH with hydrochloric acid prior to our use of the recovered regenerant solution. 4) The concentration. In the manufacturing process there is a limit to the quantity of water which may be added. The more concentrated the recovered regenerant solution, the simpler it is to recycle it to manufacturing without the incorporation of excess water. 5) The relative concentrations of potassium and dichromate. Generally the potassium content is the limiting factor as to

Table 18 **INFLUENT ANALYSES FROM NOVEMBER, 1971**

Date	**ppm** $Na_2Cr_2O_7.2H_2O$	**Date**	**ppm** $Na_2Cr_2O_7.2H_2O$
11-1	1763	11-11	1899
	1930		2231
	2478		2241
	1608	11-12	1631
11-2	1906	11-15	1426
	2647		1779
11-3	1930	11-16	2089
	2352		1724
	1864		1658
11-4	2524		1764
	1194	11-17	0965
11-5	1718		1598
	1447	11-19	1971
	1960		1945
	2020	11-22	1945
11-8	1919		2246
	1812		2382
	1839		2382
	2023	11-23	2382
	2138		*8472
11-9	1918		*15376
	2080		1357
	2005	11-24	3286
	1749		2358
	1622		2487
11-10	1764	11-26	2059
	1749		2200
	1824	11-29	1688
	1583		2517
	1667		
		Average	1952 ppm*

*** Excluding 8472 and 15,376 readings resulting from an error in pumping zinc chromate to the holding tank.**

Table 19 THE WEIGHT OF SODIUM DICHROMATE RECOVERED FROM THE RESIN COLUMNS, A MEASURE OF EXCHANGE CAPACITY

Cycle Number	Pounds Of $Na_2Cr_2O_7.2H_2O$ Recovered From IRA-900C	Pounds Of $Na_2Cr_2O_7.2H_2O$ Recovered From Dowex 1X8
1	480	965
2	602	1021
3	674	1142
4	804	753
5	509	925
6	892	705
7	633	944
8	768	1005
9	820	1101
10	717	924
11	642	939
12	766	999
13	719	982
14	738	1081
15	770	1079
16	744	999
17	650	905
18	802	923
19	620	954
20	764	1053
21	798	
Average Capacity lbs/100 cu ft	710	970

the quantity of regenerant solution which can be recycled to a given batch. No more than 4000 lbs of potassium (expressed as potassium chloride) may be recycled per batch.

As we explained in our description of the laboratory work, we have attempted to minimize the dilution of the regenerant (by rinse water), minimize the loss of potassium (via the necessary rinsing and backwashing of the resin column, and maximize the dichromate content to facilitate the recycle and prevent the accumulation of dilute solutions in storage.

In Table 20 are listed typical results of the potassium and dichromate concentrations of regenerant solutions recovered following plant use.

Table 20 TYPICAL RESULTS OF THE CONCENTRATION OF THE RECOVERED REGENERANT SOLUTIONS

	Potassium Chloride		Sodium Dichromate	
	Concentrations in g/100 ml			
Resin	Dowex 1X8	IRA-900C	Dowex	IRA-900C
Cycle No.				
1	6.960	6.173	7.265	4.440
2	7.879	6.921	7.492	5.334
3	7.053	8.095*	8.443	5.564
4	7.817	8.108	7.874	6.275
5	7.460	8.721	8.380	6.604
6	9.136*	8.651	8.565	6.614
7	7.180	6.943	8.600	6.176
8	8.391	7.660	3.252**	5.688
Ave	7.74	7.66	8.08	5.69

* Values of greater than 8% KCl result either when the column rinse used to refill the regenerant tanks contains a significant amount of potassium, or when solutions of greater than 8% are synthesized to suspend the resin to facilitate removal. See Appendix D.

** This low value was the result of a re-regeneration of a column because it was bleeding the yellow dichromate color initially. The column was not fully exhausted prior to regeneration. The low value was not included in the calculation of the average concentration.

COMPARISON BETWEEN INFLUENT DICHROMATE AND THE DICHROMATE RECOVERED IN THE REGENERANT SOLUTIONS

We were interested in comparing our recovery in the plant with the results previously obtained in the laboratory. The plant is not equipped with an integrating meter, or any continuous influent monitoring device. To determine total influent to the exchange system we sampled the influent solution approximately once per shift and analyzed each sample iodometrically for its chromate content. We recorded the flow rate to each column and the plant operators attempted to maintain this flow rate, or they recorded those periods when the flow to the system was diminished or stopped. We then accumulated influent flow in gallons and, by assuming that the sample analysis was representative of the entire interval between samples, we were able to estimate the influent chromium content as shown in Table 21.

Table 21 COMPARISON BETWEEN INFLUENT AND RECOVERED DICHROMATE IN PLANT OPERATION

Date July, 1971	Estimated Gallons Treated	Concentration Of The Influent ppm	Pounds of Sodium Dichromate In The Influent
7/1	42,700	2000	712
7/2	52,725	2000	876
7/3	61,600	2000	1027
7/7	25,200	3063	639
7/7	42,000	3060	1072
7/8	55,200	2560	1179
7/9	37,200	2306	717
7/10	54,300	2317	1049
7/12	71,000	2195	1300
7/13	30,900	2195	564
7/14	85,200	2120	1506
7/15	81,500	2743	1862
7/19	20,000	3369	562
7/21	19,950	3636	605
7/26	29,500	2032	500
7/27	25,800	1998	430
Totals	734,775 gallons		14,600 lbs

Total $Na_2Cr_2O_7.2H_2O$ in the influent	14,600 lbs
Total $Na_2Cr_2O_7.2H_2O$ recovered (From Table 23 p 77)	13,483 lbs
Difference (Recycled during rinse following regeneration and filter rinsing.)	1,117 lbs (7.7%)

Table 22 A COMPARISON OF THE DOW AND ROHM AND HAAS RESINS

	Rohm & Haas Amberlite IRA-900C	Dow Dowex 1X8
Average Volume of Influent (Gallons/100 cubic feet of resin)	44,000	59,000
Average Weight of Dichromate Recovered (Pounds $Na_2Cr_2O_7.2H_2O$/100 cubic feet)	710(1)	970(2)
Average Concentration of the Recovered Solution (Grams $Na_2Cr_2O_7.2H_2O$/100 ml.)	5.69(3)	8.08(4)

NOTES:

(1) Based on our laboratory work, we predicted between 708 and 780 pounds. (See Table 2)

(2) Laboratory results were widespread from two different resin samples. One lead us to predict 916 pounds, the other 1,257 pounds. (See Table 2)

(3) This is slightly higher than our laboratory result of 5.43. (See Table 12)

(4) Again, laboratory results varied from 7.30 to 8.70. (See Tables 13 and 14)

A SUMMARY OF TWO YEARS OF RECOVERY

The recovered regenerant solution is routinely analyzed for its potassium content by the tetraphenyl boron procedure reported in Appendix A and for its chromium content by the iodometric procedure reported in Appendix A. These potassium and chromium analyses are required before the recovered regenerant solution can be returned to the processing tanks for use in the manufacture of the zinc yellow or zinc potassium chromate pigment. Thus it was routine to record the amounts of potassium chloride and sodium dichromate recovered from the ion-exchange unit. These data are recorded in Table 23.

Table 23 is sub-divided on a monthly basis to coincide with our plant operating information. It shows the number of cycles each column has used, the quantitites of potassium chloride and sodium dichromate which were recovered from each cycle, the average quantities of these chemicals recovered from each of the resin columns and some trends, with time as a variables (i. e., an indication of resin durability or resin life.) This study accounts for 362 operating cycles, divided approximately equally between the two resins. It reports the recovery of 319,801 lbs. of potassium chloride and 337,887 lbs. of sodium dichromate over approximately a two year study period.

Table 23 A SUMMARY OF THE RECOVERY FROM THE ION-EXCHANGE SYSTEM OVER A TWO-YEAR PERIOD

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
From Start-Up Through April, 1971				
1	816	575	215	200
2	1027	600	820	432
3	1099	675	868	542
4	1000	854	971	607
5	976	1025	219	724
6	1216	810	640	458
7	1076	790	786	300
8	853	1785	599	803
Sub-Tot	8063	7114	5118	4066
Ave	1008	889	640	508
Total 16 cyc	15,177 lbs		9184 lbs	
May, 1971				
1	720	772	802	570
2	1444	693	854	691
3	1001	985	936	738
4	735	830	785	645
5	776	783	798	257
6	790	675	849	578
7	958	804	835	689
8		695		647
9		833		664
10		874		693
Sub-Tot	6424	7944	5859	6172
Ave	918	794	837	617
Total 17 cyc	14,368 lbs		12,031 lbs	
1	1359	775	1086	670
2	935	632	1079	585
3	938	833	999	722
4	1155		905	
Sub-Tot	4387	2240	4069	1977
Ave	1097	747	1017	659
Total 7 cyc	6627 lbs		6046 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
July, 1971				
1	884	776	923	558
2	1003	983	954	688
3	880	1044	1053	718
4	1113	1125	1121	783
5	957	982	1076	744
6	1125	1100	1054	849
7	996	898	1193	799
8	1077	(352)[2]	(417)[1]	553
Sub-Tot	8035	6908	7374	5692
Ave	1004	987	1053	712
Total 16 cyc	14,943 lbs		13,483 lbs	
November, 1971				
1	986	745	910	883
2	750	1000**	1131	800**
3	1045	962	1131	947
4	934	932	1182	1051
5	987	960	1194	1024
6	992	894	638*	1045
7	952	1073	761*	1086
8	948	812	1247	987
9	937		674*	
10	938		564*	
11	889		1057	
Sub-Tot	10,358	7378	10,489	7823
Ave	941	922	954	979
Total 19 cyc	17,736 lbs		19,312 lbs	
December, 1971				
1	1030	988	538	942
2	1004	970	1411	1168
3	948	901	1037	939
4	939	946	1137	1051
5	1154	877	1124	975
6	730*	878	764*	864*
7	898	935	1130	964
8	1022		1030	
Sub-Tot	7725	6495	8174	6903
Ave	966	928	1022	986
Total 15 cyc	14,220 lbs		15,077 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
January, 1972				
1	967	973	1028	924
2	989	903	1010	865
3	797	877	1041	880
4	972	887	1103	895
5	990	838	1102	837
6	1066	966	1129	727
7	1014	912	1010	758
8	987	938	1115	874
9	976	1036	1010	1006
10	1010		1113	
Sub-Tot	9768	8330	10,661	7766
Ave	977	926	1066	865
Totals 19 cyc	18,098 lbs		18,427 lbs	
February, 1972				
1	957	954	1027	960
2	1097	893	832	910
3	984	792	996	949
4	1123	998	1050	887
5	904	737	1078	884
6	955	995	1145	965
7	450	852	391	1153
8	1104	1034	1498	999
Sub-Tot	7574	7255	8017	7707
Ave	947	907	1002	963
Total 16 cyc	14,829 lbs		15,724 lbs	
March, 1972				
1	961	886	882	1039
2	1024	1055	872	943
3	864	971	873	819
4	1013	1003	991	916
5	1020	886	1074	875
6	1280	755	990	900
7	804	625	892	775
8	773	888	1000	920
9	904		1139	
Sub-Tot	8643	7069	8713	7187
Ave	960	884	968	898
Total 17 cyc	15,712 lbs		15,900 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex-1X8	IRA-900C
April, 1972				
1	928	975	1124	1047
2	1100	1044	859	1030
3	1126	884	767	1297
4	1012	801	1207	548
5	820	1029	997	1000
6	980	849	966	860
7	963	796	1098	876
Sub-Tot	6929	6378	7048	6658
Ave	990	911	1007	951
Total 14 cyc	13,307 lbs		13,706 lbs	
May, 1972				
1	908	917	1080	924
2	974	912	1040	803
3	896	915	1057	896
4	900	900	800	1056
5	900	952	1176	869
6	863	1400	966	935
7		899		1220
Sub-Tot	5441	6895	6119	6703
Ave	907	985	1020	958
Total 13 cyc	12,336 lbs		12,822 lbs	
June, 1972				
1	1025	1131	1117	535
2	781	666	1077	986
3	650	812	1037	936
4	957	652	1207	617
5	673	535	719	676
6	837	901	848	974
7	916	952	870	1109
8	945	900	872	1036
9	882	919	901	920
Sub-Tot.	7666	7468	8648	7789
Ave	852	830	961	865
Total 18 cyc	15,134 lbs		16,437 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex-1X8	IRA-900C
July, 1972				
1	895	789	1027	872
2	923	879	986	820
3	867	907	807	908
4	912	984	892	938
5	918	463	954	726
6	513		721	
Sub-Tot	5028	4022	5387	4264
Ave	838	804	898	853
Total 11 cyc	9050 lbs		9,651 lbs	
August, 1972				
1	1341	973	197	684
2	952	637	1163	820
3	876	785	935	841
4	1196	938	902	901
5	1091	940	818	893
6	985	1020	907	873
7	662	795	667	991
8	814	879	898	1019
9	856	812	785	896
10	965	828	748	812
11	1003		881	
Sub-Tot	10,741	8607	8901	8730
Ave	976	861	809	873
Total 21 cyc	19,348 lbs		17,631 lbs	
September, 1972				
1	913	990	924	803
2	952	843	1040	951
3	904	900	874	800
4	939	917	924	993
5	952	854	889	927
6	956	985	766	1037
7	938	850	799	899
8	795	806	788	880
9	897	864	832	944
10	874	831	864	900
11		944		815
Sub-Tot	9120	9784	8700	9949
Ave	912	889	870	904
Totals 21 cyc	18,904 lbs		18, 649 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
October, 1972				
1	866	833	983	772
2	918	701	1307	930
3	856	1061	1278	966
4	881	830	1206	987
5	964	766	1421	948
6	841	877	1315	1085
7	900	800	800	1000
8	891	834	932	852
9	883	745	1211	842
10	732	1070	857	602
Sub-Tot	8732	11,310	8517	8984
Ave	873	1131	852	898
Total 20 cyc	17,249 lbs		20,294 lbs	
November, 1972				
1	802	812	1216	1135
2	775	800	1204	1211
3	807	770	1037	945
4		764		1111
Sub-Tot	2384	3146	3457	4402
Ave	795	787	1152	1100
Total 7 cyc	5,530 lbs		7,859 lbs	
December, 1972				
1	861	759	988	1008
2	893	1294	654	989
3	903	699	1223	1112
4	1079	1007	1457	904
5	944		803	
6	1526		1801	
7				
8	934		1047	
Sub-Tot	7140	3119	8613	4013
Ave	892	780	1077	1003
Total 12 cyc	10,259 lbs		12,626 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
January, 1973				
1	967	976	1245	1166
2	527	823	642	705
3	1045	745	1594	1201
4	854	906	1327	1113
5	816	779	1175	1206
6	821	682	1110	1025
7	797	750	1072	1021
8	785	771	1167	1135
9		647		1091
Sub-Tot	6612	7079	9332	9663
Ave	827	787	1167	1074
Total 17 cyc	13,691 lbs		18,995 lbs	
February, 1973				
1	888	816	1255	1131
2	823	759	1248	1187
3	727	663	845	847
4	750	771	1030	988
5	466	749	90	750
6	812	808	800	623
7	889	796	1127	1055
8	805		945	
9	1126		1140	
Sub-Tot	7285	5362	8480	6581
Ave	809	766	942	940
Total 16 cyc	12,647 lbs		15,061 lbs	
March, 1973				
1	861	715	1355	1162
2	761	823	1050	1196
3	821	587	1171	533
4	784	717	1138	1049
5	747	795	1040	1026
6	911	615	1265	668
7	730	818	946	623
8	776	785	1073	686
9	750	811	1147	1200
10	759	695	1097	1127
Sub-Tot	7900	7461	11,282	9270
Ave	790	746	1128	927
Total 20 cyc	15,361 lbs		20,552 lbs	

Table 23 (CONTINUED)

Cycle No.	KCl Recovered Pounds		$Na_2Cr_2O_7.2H_2O$ Recovered	
	Dowex 1X8	IRA-900C	Dowex 1X8	IRA-900C
April, 1973				
1	937	754	1340	874
2	827	736	980	991
3	948	746	761	994
4	1055	773	895	999
5	836	868	1055	847
6	746	536	580	670
7	1137	996	1456	1238
8	954	945	580	1056
9	912	743	811	926
10		947		943
Sub-Tot	8352	8044	8458	9538
Ave	928	804	940	954
Total 19 cyc	16,396 lbs		17,996 lbs	
May, 1973				
1	927	835	899	721
2	761	794	453	1055
3	1095	958	1526	1246
4	444	849	587	1042
5	1063	766	1436	878
6	377		587	
Sub-Tot	4667	4204	5488	4942
Ave	778	840	915	988
Total 11 cyc	8,869 lbs		10,430 lbs	

SUMMARY

	Cycles	Pounds of KCl Recovered	Pounds of $Na_2Cr_2O_7.2H_2O$ Recovered
April, 1971	16	15,177	9,184
May	17	14,368	12,031
June	7	6,627	6,046
July	16	14,943	13,483
November*	19	17,736	19,312
December	15	14,220	15,077
January, 1972	19	18,098	18,427
February	16	14,829	15,724
March	17	15,712	15,900
April	14	13,307	13,700
May	13	12,336	12,822
Sub-Total	169	157,353	151,706

Table 23 (CONTINUED)

SUMMARY

	Cycles	Pounds of KCl Recovered	Pounds of $Na_2Cr_2O_7.2H_2O$ Recovered
June, 1972	18	15,134	16,437
July	11	9,050	9,651
August	21	19,348	17,631
September	21	18,904	18,649
October	20	17,249	20,294
November	7	5,530	7,859
December	12	10,259	12,626
January, 1973	17	13,691	18,995
February	16	12,647	15,061
March	20	15,361	20,552
April	19	16,396	17,996
May	11	8,869	10,430
Sub-Total	193	162,448	186,181
Total	362	319,801	337,887

* The system was down for three months to accomplish extensive repairs and revisions to the resin columns.

APPENDIX D

USEFUL INFORMATION FOR DESIGNERS AND OPERATORS

TYPICAL OPERATING PARAMETERS

	Lab Scale	Plant Scale
The Influent		
Chrome Conc. ($Na_2Cr_2O_7.2H_2O$)	1840 ppm	.0153 lb/gal
Chloride Conc. (NaCl)	21.0 g/l or 0.36 mol/l	.175 lb/gal
Density @25°C	1.015 g/cc	
Viscosity @25°C	5.5 cps	
Volume	from 50,000 to 80,000 gal/day or 2100 to 3600 gal/hr or 35 to 60 gpm	
The Recovered Regenerant Solution (Combined Portions I and II)		
Chrome Conc. ($Na_2Cr_2O_7.2H_2O$)		
Dowex 1X8	8.70 g/100 ml	.726 lb/gal
Amberlite IRA-900C	7.30	.609
Potassium Conc. (KCl)	7.87	.656
Density @30°C	1.08 to 1.10 g/cc	
The Original Regenerant Solution		
Volume	4 x 100 ml	4 x 750 gal
Composition		
NaOH	4 g/100 ml	250 lbs/750 gal
KCl	8 g/100 ml	500 lbs/750 gal
Density @43°C	1.0764 g/cc	
@38°C	1.0796 g/cc	
Viscosity @40°C	10 cps	
The Ion-Exchange Resin		
Exchange Capacity		
Dowex 1X8	14.7 to 20.1 g/100 ml	916 to 1257 lbs/100 cu ft
Amberlite IRA-900C	11.4 to 12.5	708 to 780
Volume Normally Used	100 ml	100 cu ft
Treatment Flow Rate	15 to 20 ml/min	40 to 60 gpm
Backwash Flow Rate	20 to 40	25-50
Regenerant Flow Rate	3 to 6	25 to 50
Rinse Volume	1000 ml	to 7500 gal

	Lab Scale	Plant Scale
Hydrochloric Acid Requirement		
To adjust influent from pH 6.3 to 3.0		1000 - 1200 lbs/day
To acidify the resin column following regeneration		to 300 lbs/day
Sodium Carbonate Requirement		
To precipitate zinc carbonate by adjusting pH from 3.0 to 9.0		to 800 lbs/day

CONVERSION FACTORS

To Convert From	To	Multiply By
g/100 ml	lbs/cu ft	0.6243
g/100 ml	lbs/gal	0.08345

CALCULATION OF EXCHANGE COEFFICIENTS FOR THE ION-EXCHANGE RESINS

In the Discussion section we touched briefly on the applicability of this system to other industries. Doubtlessly, the surest way to ascertain this applicability is by careful laboratory experimentaion. It is often helpful to be able to justify such a research program initially. One approach is by the use of meaningful calculations.

The exchange of dichromate for chloride ion on the ion-exchange resin is an equilibrium process, and, as indicated by Kunin[20], it should be possible to calculate a selectivity constant or an exchange coefficient. With the aid of an exchange coefficient it would appear that one could then estimate such values as: What is the maximum permissable level of chloride ion in the influent for satisfactory exchange to occur? How much of the adsorbed dichromate must be removed from the resin during regeneration in order to assure a water-white effluent? If one has an intermediate regenerant solution which contains x moles of dichromate per liter, should this be used for a further regeneration, or should it be recycled to manufacturing?

We will describe here our calculation of the exchange coefficients and give some examples for their use.

From the equation representing adsorption of dichromate on a resin in the chloride form, i.e., equation (5)

$$Cr_2O_7^{=} + 2\ \text{Resin Cl} \rightleftharpoons (\text{Resin})_2\,Cr_2O_7 + 2Cl^- \qquad (5)$$

an exchange coefficient for the treatment step can be written as equation (7), where the [ ] represents the concentration expressed in moles per liter.

$$K = \frac{\left[Cr_2O_7^{=} Resin\right]}{\left[Cr_2O_7\ Sol'n\right]} \quad \frac{\left[Cl^- Sol'n.\right]^2}{\left[Cl^-\ Resin\right]^2} \qquad (7)$$

1.

a. For the Rohm and Haas IRA-900C resin during treatment with an influent pH between 2.2 and 2.5, as indicated in Table 2 an average loading at exhaustion is 11 g/100 ml resin. This is equivalent to 0.367 mole/liter.

Thus $\left[Cr_2O_7^{=}Resin\right] = 0.367$ mole/liter

b. This implies that 0.367 x 2 or 0.734 mole of Cl^- is released from the resin to solution during treatment. If the volume to exhaust the column is 6300 ml., then .734/6.3 liters = 0.117 mole NaCl/liter is the increase in the NaCl concentration.

The concentration of NaCl coming to the resin column is approximately 0.36 mole/liter, so the concentration of NaCl leaving the resin tower is therefore approximately 0.477 mole/liter and

$$\left[Cl^-\ Sol'n.\right]^2 = \left[.477\right]^2 = .2275\ (moles/liter)^2$$

c. According to the data from Rohm & Haas[9] the minimum capacity of the IRA-900C resin is 1 mole/liter. From our data it would appear that a reasonable figure would be 1.115 mole/liter. If, during treatment, 0.734 mole has been exchanged for Cr_2O_7, this leaves 0.381 mole of chloride ion remaining on the resin and

$$\left[Cl^-Resin\right]^2 = \left[0.381\right]^2 = 0.145\ (moles/liter)^2$$

d. The dichromate content leaking from the column toward the end of the exhaustion cycle was determined to be 0.000712 mole/liter, and

$$\left[Cr_2O_7^{=}Sol'n\right] = 0.000712\ (moles/liter)^2$$

Therefore

$$K_{R\&H} = \frac{(.367)(.2275)}{(.000712)(.145)} = 808.7$$

2.

a. For the Dowex 1X8 resin a typical loading is 14g/100 ml of resin or

$$\left[Cr_2O_7^{-}\ Resin\right] = 0.470\ mole/liter$$

b. This implies 0.470 x 2 = 0.940 mole of Cl^- were released from the resin to solution during treatment. Since 7840 ml of influent were required to exhaust the column,

$$.940/7.84 = 0.1199 \text{ mole/liter.}$$

Again, since the NaCl content of the influent is 0.36 mole/liter, the concentration of NaCl leaving the resin column is 0.480 mole/liter and

$$\left[Cl^- \text{ Sol'n}\right]^2 = (.480)^2 = (.230)\ (\text{mole /liter})^2$$

c. From the Dow data sheet on Dowex 1X8, the capacity of the resin is approximately 1.4 moles/liter. If during treatment 0.940 mole of chloride is exchanged for dichromate, then 1.400 - 0.940 = 0.460 mole of chloride remain per liter and

$$\left[Cl^- \text{ Resin}\right]^2 = (0.460)^2 = .2116\ (\text{mole /liter})^2$$

d. As in 1d.

$$\left[Cr_2O_7^= \text{ Sol'n}\right] = 0.000712$$

$$K_{DOW} = \frac{(.230)(.470)}{(7.12\text{x}10^{-4})(.2116)} = 718$$

Sample Calculations:

1. Using $K_{R\&H} = 809$ calculate $\left[Cr_2O_7^= \text{ Sol'n}\right]$ at the point of leaking from the column.

From our operating data we found 4000 ml. of influent which contained an average of 7.50g sodium dichromate was sufficient to "bleed" beyond a water-white effluent.

7.50g Sodium dichromate/100 ml or

$$0.2517 \text{ mole/liter} = \left[Cr_2O_7^= \text{ Resin}\right]$$

Again, if 0.25 mole of sodium dichromate is exchanged, 0.50 mole of Cl^- is removed from the resin to the effluent. 0.50 mole/4 liters = 0.125 mole mole NaCl/liter added to the original 0.36 mole/liter = 0.485 mole NaCl/liter = $\left[Cl^- \text{ Sol'n}\right]$

If the original $\left[Cl^-\right]$ on the resin is 1.115 mole/liter, and we have removed 0.50 mole, there is 0.165 mole remaining

and $\left[Cl^- \text{ resin}\right] = 0.615$ mole/liter

Therefore

$$809 = \frac{(.485)^2(.25)}{(Cr_2O_7^{=}\text{sol'n.})(.615)^2}$$

$$\left[Cr_2O_7^{=}\ \text{Sol'n}\right] = 1.92 \times 10^{-4}\ \text{moles/liter}$$

$$809 = \frac{(0.372)^2\ (0.45)}{\left[Cr_2O_7^{=}\text{sol'n}\right]\ (.215)^2}$$

or, rearranging

$$\left[Cr_2O_7^{=}\ \text{sol'n}\right] = .00167\ \text{mole/liter}$$

Thus, the effluent concentration at "exhaustion" would have decreased from 1,840 g sodium dichromate/liter to 0.498 g/liter.

This is equivalent to 1.00×10^{-3}g. Cr/liter or 1.00 ppm in good agreement with our observation that 1 ppm is colorless and 2-5 ppm are required to detect the yellow color visually in a 4 oz. jar sample.

2. Using K=809, calculate the maximum allowable Cl^- to exchange $Cr_2O_7^{=}$ if the influent concentration is 2400 ppm, and regeneration removes $Cr_2O_7^{=}$ to a level of 0.004 mole sodium dichromate/liter of resin. 2400 ppm is equivalent to 0.00805 mole of sodium dichromate per liter.

$$809 = \frac{Cl^-\ \text{sol'n.}^{\ 2}\ (.004)}{(.00805)(1.142)^2}$$

$$(Cl^-)^2 = \frac{(809)(.00805)(1.304)}{(.004)}$$

$$(Cl^-)^2 = 2123$$

$$(Cl^-) - 46$$

Thus chloride concentrations of 0.36 to 0.50 mole/liter should never present a problem if the regeneration is satisfactory.

3. If 1840 ppm influent is being treated, what is the effluent concentration from this column-at "exhaustion" if we assume a maximum loading of 0.45 mole sodium dichromate per liter of resin?

$$\frac{1.840\text{g. } Na_2Cr_2O_7.2H\ O\text{/liter}}{298} = .00617\ \text{mole/liter}$$

$$\frac{0.45\ \text{mole}}{.00617\ \text{mole/liter}} = 73.0\ \text{liters of influent}$$

would have been treated by the one liter of ion exchange resin at the time of exhaustion.

If 0.90 mole of Cl^- has been released from the resin into 73.0 liters, the average increase in the chloride content of the resin effluent is

$$\frac{0.90}{73} = 0.0.23 \text{ mole } Cl^-/\text{liter}$$

0.36 + 0.0123 = 0.372 mole/liter = Cl^- sol'n.). Again, if the original Cl^- content of the resin is 1.115 mole/liter, and 0.90 mole has been removed in the exchange, then Cl^- resin =0.215 moles/liter.

We have mentioned from time to time the technique of suspending the ion-exchange resin in a salt solution so that it can be pumped with minimum attrition or damage to the resin beads. Figure 21 was made up from data taken from the Handbook of Chemistry and Physics, 45th Edition, and shows the relationship between the percentage composition of a potassium chloride solution and its density. Also shown in the figure are the densities of the two ion-exchange resins under study here.

If the density of the salt solution is greater than the density of the ion-exchange resin, then the resin will float in the solution. Generally the resin is handled most easily if it is suspended in a solution in which it will settle, but only very slowly, because of a very slight difference in the densities of the resin and the suspending salt solution. Agitation from the action of the diaphragm pump is usually sufficient to maintain the resin in suspension.

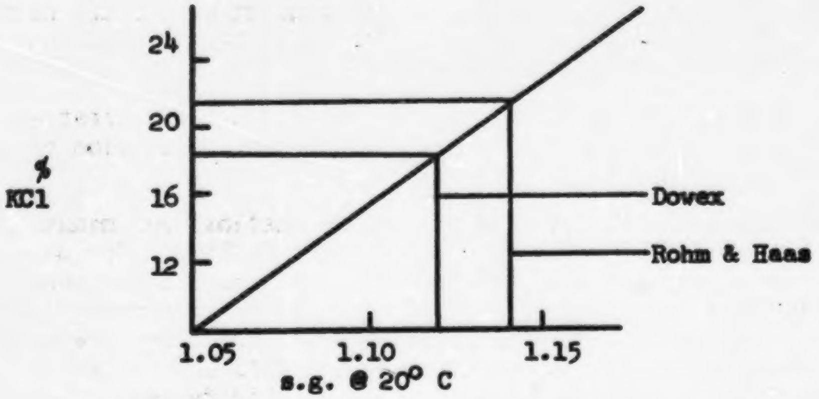

Figure 21 PLOT OF THE CONCENTRATION OF POTASSIUM CHLORIDE SOLUTIONS AND THEIR SPECIFIC GRAVITIES